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# National Surface Water Survey: Eastern Lake Survey (Phase 1 - Synoptic Chemistry). Analytical Methods Manual

Lockheed Engineering and Management
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# NATIONAL SURFACE WATER SURVEY
# EASTERN LAKE SURVEY (PHASE I - SYNOPTIC CHEMISTRY)
# ANALYTICAL METHODS MANUAL

by

D. C. Hillman, J. F. Potter,
and S. J. Simon
Lockheed Engineering and Management Services Company, Inc.
Las Vegas, Nevada 89114

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Project Officer

E. P. Meier
Advanced Monitoring Systems Division
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada 89114

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89114

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**16. ABSTRACT**

The National Surface Water Survey (NSWS) of the National Acid Precipitation Assessment Program is a three-phase project to evaluate the current water chemistry of lakes and streams, determine the status of fisheries and other biotic resources, and select regionally representative surface waters for a long-term monitoring program. This manual provides details of the analytical methods and internal quality control used to process and analyze samples for Phase I of the Eastern Lake Survey.

Analytical protocols are given for 23 chemical parameters commonly of interest in surface water studies and considered to be applicable to acid deposition investigations. The methods are generally adapted from, "Methods for Chemical Analysis of Water and Wastes," EPA 600/4-79-020 and, "Standard Methods for the Examination of Water and Wastewater," the American Public Health Association. An expert workshop was held for the identification and selection of appropriate methods, and in cases where equivalency of method performance existed, cost and time savings governed the selection. A choice of methods (flame AAS, ICP) is given for several of the cations under the condition that the required instrumental detection limits are achieved.

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The mention of trade names or commercial products in this manual is for illustration purposes and does not constitute endorsement or recommendation for use.

# ABSTRACT

The National Surface Water Survey of the National Acid Precipitation Assessment Program is a three-phase project to evaluate the current water chemistry of lakes and streams, determine the status of fisheries and other biotic resources, and select regionally representative surface waters for a long-term monitoring program to study changes in aquatic resources. The Eastern Lake Survey is part of Phase I of the National Surface Water Survey lake study.

The U.S. Environmental Protection Agency requires that data collection activities be based on a program which ensures that the resulting data are of known quality and are suitable for the purpose for which they are intended. In addition, it is necessary that the data obtained be consistent and comparable throughout the survey. For these reasons, the same reliable, detailed analytical methodology must be available to and used by all analysts participating in the study.

This manual provides details of the analytical methods and internal quality control used to process and analyze samples for the Eastern Lake Survey. The determinations and methods described are the following:

| Parameter | Method |
|---|---|
| 1. Acidity | Titration with Gran analysis |
| 2. Alkalinity | Titration with Gran analysis |
| 3. Aluminum, total | 202.2 AAS (furnace) |
| 4. Aluminum, total extractable | Extraction with 8-hydroxyquinoline into MIBK followed by AAS (furnace) |
| 5. Ammonium, dissolved | Automated colorimetry (phenate) |
| 6. Calcium, dissolved | AAS (flame) or ICPES |
| 7. Chloride, dissolved | Ion chromatography |
| 8. Fluoride, total dissolved | Ion-selective electrode and meter |
| 9. Inorganic carbon, dissolved | Instrumental (acidification, $CO_2$ generation, IR detection) |
| 10. Iron, dissolved | AAS (flame) or ICPES |
| 11. Magnesium, dissolved | AAS (flame) or ICPES |
| 12. Manganese, dissolved | AAS (flame) or ICPES |
| 13. Nitrate, dissolved | Ion chromatography |
| 14. Organic carbon, dissolved | Instrumental (uv-promoted oxidation, $CO_2$ generation, IR detection) |
| 15. pH | pH electrode and meter |
| 16. Phosphorus, total | Automated colorimetry (phosphomolybdate) |

| Parameter | Method |
|---|---|
| 17. Potassium, dissolved | AAS (flame) |
| 18. Silica, dissolved | Automated colorimetry (molybdate blue) |
| 19. Sodium, dissolved | AAS (flame) |
| 20. Sulfate, dissolved | Ion chromatography |
| 21. Specific conductance | Conductivity cell and meter |
| 22. True color | Comparison to Platinum-Cobalt color standards |
| 23. Turbidity | Instrumental (nephelometer) |

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## 1.0 INTRODUCTION

The National Surface Water Survey (NSWS) is divided into two major components (Figure 1.1), the National Lake Survey (NLS) and the National Stream Survey (NSS), each of which has three phases.

### 1.1 Background

Phase I of the Eastern Lake Survey (ELS-I) is part of the NSWS and involves a synoptic chemical survey of 1,800 lakes in the Eastern United States. The NSWS program is part of the National Acid Precipitation Assessment Program (NAPAP). One of the responsibilities of NAPAP is to assess the extent and severity to which aquatic resources within the U.S. are at risk due to effects of acidic deposition. The NSWS was initiated at the request of the Administrator of EPA when it became apparent that existing data could not be used to quantitatively assess the present chemical and biological status of surface waters in the U.S.

Extrapolation of existing data, largely compiled through individual studies, to the regional or national scale was limited because studies were often biased in terms of site selection. Additionally, many previous studies were incomplete with respect to the chemical variables of interest, inconsistent relative to sampling/analytical methodologies, or highly variable in terms of data quality.

The ELS-I was designed to alleviate uncertainty in making regional assessments based on existing data by:

(1) providing data from a subset of lakes which are characteristic of the overall population of lakes within a region;

(2) using standardized methods in collection of chemical data;

(3) measuring a complete set of variables thought to influence or be influenced by surface-water acidification;

(4) providing data which can be used to statistically investigate relationships among chemical variables on a regional basis; and

(5) providing reliable estimates of the chemical status of lakes within a region of interest.

The U.S. Environmental Protection Agency (EPA) requires that data collection activities be based on a program which ensures that the resulting data are of known quality and are suitable for the purpose for which they are

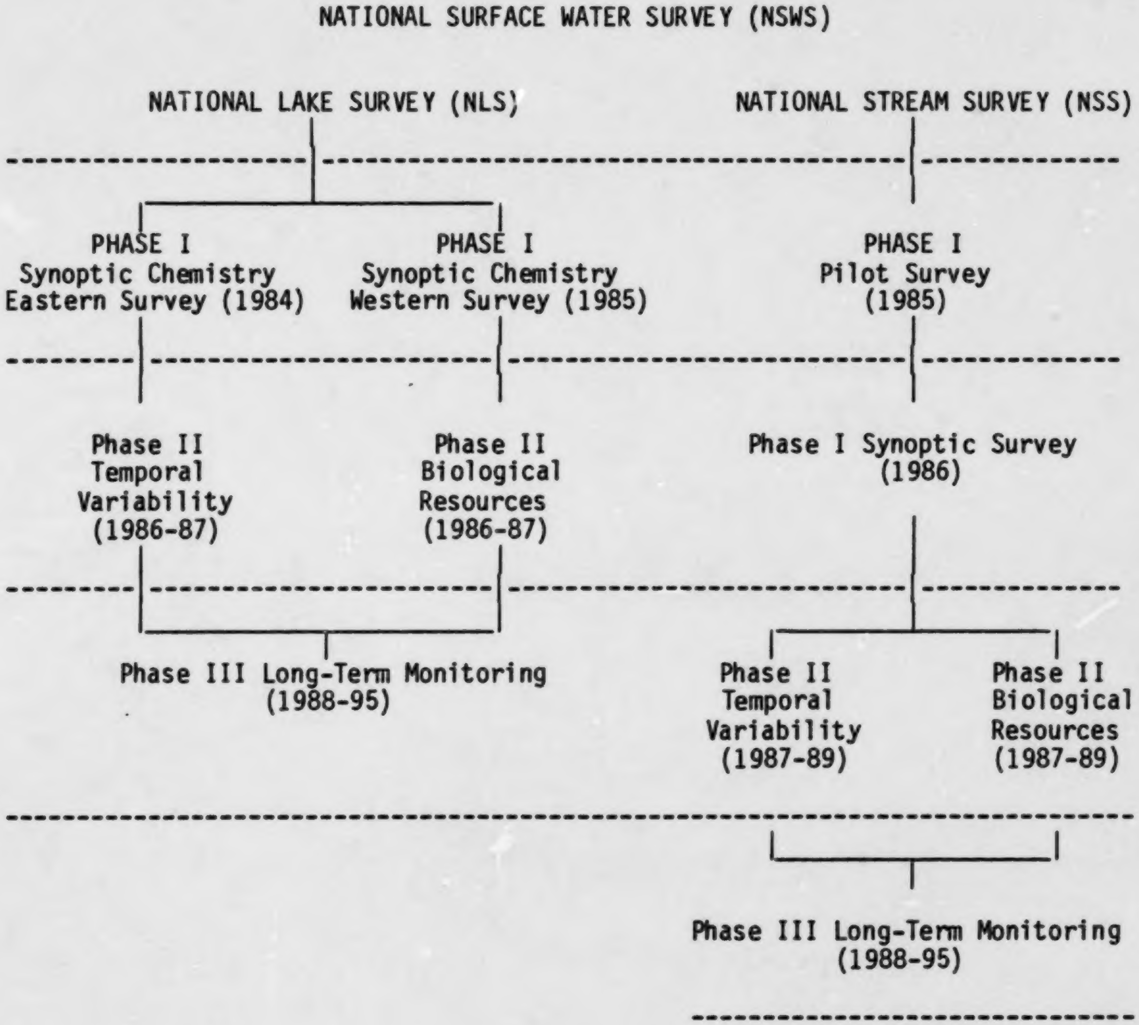

NATIONAL SURFACE WATER SURVEY (NSWS)
NATIONAL LAKE SURVEY (NLS)
NATIONAL STREAM SURVEY (NSS)
PHASE I Synoptic Chemistry Eastern Survey (1984)
PHASE I Synoptic Chemistry Western Survey (1985)
PHASE I Pilot Survey (1985)
Phase II Temporal Variability (1986-87)
Phase II Biological Resources (1986-87)
Phase I Synoptic Survey (1986)
Phase III Long-Term Monitoring (1988-95)
Phase II Temporal Variability (1987-89)
Phase II Biological Resources (1987-89)
Phase III Long-Term Monitoring (1988-95)

Figure 1.1. Organizational diagram of the National Surface Water Survey and the years during which field activities are to be initiated.

intended. The EPA's goals in designing the ELS-I were to clearly identify ELS-I objectives; identify intended uses and users of the data; develop an overall conceptual and practical approach to meeting the objectives; develop an appropriate survey design; identify the quality of data needed; develop analytical protocols and quality assurance/quality control (QA/QC) procedures; test the approach through a "pilot" or feasibility study; and revise and modify the approach and methodology as needed.

Using these criteria as guidelines, ELS-I was designed to provide statistically comparable data which could be extrapolated with a known degree of confidence to a regional or national scale. The conceptual approach to the survey emphasized that the data would not be used to ascribe observed effects to acidic deposition phenomena. Rather, the survey's intent was to provide information for developing of correlative, not cause-and-effect, relationships through large-scale monitoring activities.

The conceptual approach to the program was developed by EPA personnel and cooperating scientists. Planning for the ELS-I began in October 1983. The research plan for the National Surface Water Survey, National Lake Survey Phase I (U.S. EPA, 1984) was initially reviewed late in 1983 by 100 scientists who have expertise in the areas of study. Fifty scientists discussed the plan during a workshop held in December; suggested modifications were incorporated by March 1984. The Research Plan was submitted to members of the American Statistical Association (ASA) for review in June 1984; a final ASA review was conducted in October.

The National Surface Water Survey Eastern Lake Survey (Phase I - - Synoptic Chemistry) Quality Assurance Plan (Drousé et al., 1986) provides details of the extensive external and internal QA and QC activities.

This manual provides details of the analytical methods and internal QC used to process and analyze the lake samples. Details of the actual sampling and on-site lake analyses are provided in the field operations report (Morris et al., 1986).

## 1.2 Physical Parameters and Analytes Measured

The constituents and parameters to be measured, along with a rationale for each, are listed below. Table 1.1 lists the required detection limits, relative precision goals, and expected concentration ranges.

### 1.2.1 $CO_2$ Acidity (acidity)

$CO_2$ acidity is the base neutralizing capacity (BNC, the quantity of OH ions reacted over a given pH range during a base titration) of a carbonate system. The lakes sampled for the NSWS can generally by described by a

TABLE 1.1. REQUIRED MINIMUM ANALYTICAL DETECTION LIMITS, EXPECTED RANGES, AND INTRALAB RELATIVE PRECISION

| Parameter[a] | Units | Required Detection Limit | Expected Range | Relative Intralab Precision Goal (%)[b] |
|---|---|---|---|---|
| Acidity | µeq/L | - | 10-150 | 10 |
| Alkalinity | µeq/L | - | -100-1000 | 10 |
| Al, Total Extractable | mg/L | 0.005 | 0.005-1.0 | 10(Al>0.01),20(Al<0.01) |
| Al, Total | mg/L | 0.005 | 0.005-1.0 | 10(Al>0.01),20(Al<0.01) |
| Ca | mg/L | 0.01 | 0.5-20 | 5 |
| $Cl^-$ | mg/L | 0.01 | 0.2-10 | 5 |
| DIC | mg/L | 0.05 | 0.05-15 | 10 |
| DOC | mg/L | 0.1 | 0.1-50 | 5(DOC>5),10(DOC<5) |
| $F^-$, Total | mg/L | 0.005 | 0.01-0.2 | 5 |
| Fe | mg/L | 0.01 | 0.01-5 | 10 |
| K | mg/L | 0.01 | 0.1-1 | 5 |
| Mg | mg/L | 0.01 | 0.1-7 | 5 |
| Mn | mg/L | 0.01 | 0.01-5 | 10 |
| Na | mg/L | 0.01 | 0.5-7 | 5 |
| $NH_4^+$ | mg/L | 0.01 | 0.01-2 | 5 |
| $NO_3^-$ | mg/L | 0.005 | 0.01-5 | 10 |
| P, Total | mg/L | 0.002 | 0.005-0.07 | 10(P>0.01),20(P<0.01) |
| pH, Field | pH units | - | 3-8 | ±0.1[c] |
| pH, Lab | pH units | - | 3-8 | ±0.05[c] |
| $S_iO_2$ | mg/L | 0.05 | 2-25 | 5 |
| $SO_4^{2-}$ | mg/L | 0.05 | 1-20 | 5 |
| Specific Conductance | µS/cm | [d] | 5-1000 | 1 |
| True Color | PCU[e] | 0 | 0-200 | ±5[c] |
| Turbidity | NTU | 2 | 2-15 | 10 |

[a] Dissolved ions and metals are being determined, except where noted.
[b] Unless otherwise noted, this is the relative precision at concentrations above 10 times instrumental detection limits.
[c] Absolute precision goal is in terms of applicable units.
[d] Blank must be <0.9 µS/cm.
[e] PCU = platinum-cobalt units.

carbonate system, i.e., a sample in which the soluble reacting protolytes are the carbonate species ($H_2CO_3$, $HCO^-_3$, and $CO_3^{2-}$) as well as $H^+$ and $OH^-$. In conjunction with alkalinity, this measurement is useful in refining calculations for both alkalinity and acidity. (An iterative calculation procedure is performed. During each iteration, improved values for alkalinity and acidity are generated).

### 1.2.2 Alkalinity

Alkalinity is the acid neutralizing capacity (ANC, the quantity of H ions reacted over a given pH range during an acid titration) of a carbonate system. Because of its inherent relationship to buffering capacity, alkalinity is an important variable in acid deposition studies.

### 1.2.3 Aluminum, Total Extractable

The determination of total extractable aluminum provides an estimate of dissolved aluminum and includes most mononuclear aluminum species. Aluminum is considered to be highly toxic, especially to fish. Knowing its concentration is important in assessing the biological environment of a lake.

### 1.2.4 Aluminum, Total

Total aluminum is an estimate of the potential aluminum pool available to the biological environment.

### 1.2.5 Dissolved Inorganic Carbon

The field determination of dissolved inorganic carbon (DIC) is useful in determining the degree of dissolved $CO_2$ saturation in a lake. Both the field and lab determinations of DIC (combined with pH) are useful in QA/QC calculations.

### 1.2.6 Dissolved Ions (Na, K, Ca, Mg, Fe, Mn, $NH_4^+$, $F^-$, $Cl^-$, $SO_4^{2-}$, and $NO_3^-$)

The determination of major ions is necessary in order to chemically characterize a lake. For example, fluoride is important as an aluminum chelator.

The determinations are also valuable in QA/QC calculations for mass ion and conductivity balances.

### 1.2.7 Dissolved Organic Carbon

Dissolved organic carbon (DOC) determination is necessary to establish a relationship with color and to estimate the concentration of organic acids. Also, DOC is important as a natural chelator of aluminum.

### 1.2.8 Dissolved Silica ($SiO_2$)

The absence or existence of dissolved silica is an important factor controlling diatom blooms, and it assists in identifying trophic status. It is also an indication of mineral weathering.

### 1.2.9 pH

pH is a general and direct indication of free hydrogen ion concentration.

### 1.2.10 Specific Conductance

The specific conductance of lake water is a general indication of its ionic strength and is related to buffering capacity.

### 1.2.11 Total Phosphorus

Total phosphorus is an indicator of potentially available nutrients for phytoplankton productivity and overall trophic status.

### 1.2.12 True Color

True color indicates the presence of organic acids and DOC. Substances which impart color may also be important natural chelators of aluminum.

### 1.2.13 Turbidity

Turbidity is a measure of suspended material in a water column.

## 1.3 References

Drousé, S. K., D. C. Hillman, L. W. Creelman, and S. J. Simon, 1986. National Surface Water Survey. Eastern Lake Survey (Phase I - Synoptic Chemistry) Quality Assurance Plan. U.S. Environmental Protection Agency, Las Vegas.

Morris, F. A., D. V. Peck, D. C. Hillman, K. J. Cabble, M. B. Bonoff, S. L. Pierett, 1986. National Surface Water Survey. Eastern Lake Survey (Phase I - Synoptic Chemistry) Field Operations Report. U.S. Environmental Protection Agency, Las Vegas.

U.S. Environmental Protection Agency, 1984. National Surface Water Survey. National Lake Survey - Phase I. NAPAP Project Reference No. E-23. U.S. EPA, Office of Research and Development, Washington, D.C.

# 2.0 FIELD OPERATIONS

Field operations are based at fully equipped mobile field laboratories, or field stations. A list of equipment contained in the field station is given in Table 2.1. Lake samples, collected by sampling crews, are delivered to the field station for preliminary analysis, processing, and shipment to analytical laboratories for more detailed analysis.

The activities of the field station crew are described in this section. Sampling crew activities are described elsewhere (Morris et al., 1986).

## 2.1 Personnel

The field station is staffed by a five-person crew consisting of a coordinator, supervisor, and three analysts. The coordinator is responsible for the overall operation of the field station including coordination with the sampling crews, communication with the EPA's Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV), sample tracking and logistics, data forms, and safety. The supervisor, with the assistance of the analysts, is responsible for field station measurements and sample processing.

## 2.2 Daily Operation

The field station operates each day that samples are collected. The daily field station activities (outlined in Figure 2.1) are based upon samples arriving at about 4:00 p.m. each day. The daily operations are divided into activities that are conducted before sample arrival (discussed in section 2.2.1) and activities that are conducted following sample arrival (discussed in section 2.2.2).

### 2.2.1 Activities Before Sample Arrival

Prior to sample arrival, the reagents for determining DIC, determining pH, and preparing aliquot 2 (total extractable Al) are prepared as described in sections 2.3, 2.4, and 2.7, respectively. Also, the carbon analyzer, pH meter, and nephelometer are calibrated as described in sections 2.3, 2.4, and 2.5, respectively.

### 2.2.2 Activities Following Sample Arrival

After samples are delivered by the sampling crews, the steps outlined in Figure 2.1 are performed. The first step, performed by the coordinator, involves organizing the samples into a batch. The next five steps (aliquot preparation and pH, DIC, color, and turbidity determinations) are performed simultaneously by the supervisor and three analysts. Finally, after all measurements and processing are finished, the data forms are completed, the samples are packed, and the forms and samples

### TABLE 2.1. FIELD STATION EQUIPMENT LIST

| | |
|---|---|
| 1. Mobile Lab Equipped with | |
| a. Electrical and water inputs | |
| b. Water outlet | |
| c. Source of water meeting ASTM Type I specifications (such as Barnstead NANOpure/ROpure 40 or Millipore Milli-RO/Super-Q System) | |
| d. Heating/cooling system | |
| e. Freezer | |
| f. Laminar flow hood delivering class 100 air | |
| g. Solvent storage cabinet | |
| h. Standard laboratory countertops and sink | |
| i. Analytical balance and plastic weighing boats | |
| 2. Centrifuge (capable of holding four 50-mL tubes) | - 1 |
| 3. Clean 4-L Cubitainers | - 30/day |
| 4. Clean Nalgene Amber Wide-Mouth Bottles | |
| a. 500-mL (Nalgene No. 2106-0016) | - 30/day |
| b. 250-mL (Nalgene No. 2106-0008) | - 60/day |
| c. 125-mL (Nalgene No. 2106-0004) | - 90/day |
| 5. Total Extractable Aluminum Supplies | |
| a. Clean 50-mL graduated centrifuge tubes with sealing caps (Fisher No. 05-538-55A) | - 30/day |
| b. Clean 10-mL centrifuge tubes (Nalgene 3119-0010) | - 30/day |
| c. Clean sealing caps for 10-mL centrifuge tubes (Nalgene 3131-0013) | - 30/day |
| d. HPLC-grade methyl isobutyl ketone (MIBK) | - 180 mL/day |
| e. Sodium acetate (Alfa ultrapure) | - 80 g/month |
| f. 8-hydroxyquinoline ($99^+$% purity) | - 30 g/month |
| g. $NH_4OH$ (30% - Baker Instra-Analyzed grade) | - 750 mL/month |
| h. Clean 1-L, 500-mL, and 100-mL volumetric flasks | - 5 of each |
| i. Glacial acetic acid (Baker Instra-Analyzed grade) | - 100 mL/month |
| j. Hydrochloric acid (12 M - Baker Instra-Analyzed grade) | - 500 mL/month |
| k. Phenol-red indicator solution (0.04% w/v - American Scientific Products 5720) | - 1 L |
| l. 2.00-mL Repipet dispenser | - 2/station |
| m. 3.00-mL Repipet dispenser top for 1-gallon bottle | - 2/station |
| n. 5.00-mL Repipet dispenser | - 2/station |
| o. 100-mL reagent bottle with dropper (Nalgene 2411-0060) | - 2/station |
| p. Polystyrene graduated cylinders (25-, 100-, 250-mL sizes) | - 2 each/station |

(continued)

TABLE 2.1. (Continued)

| | | |
|---|---|---|
| 6. | Color Determination Kit (Hach Model CO-1) | - 2 |
| 7. | Color Kit Spare Supplies | |
| | a. Color disc (Hach No. 2092-00) | - 2 |
| | b. Color viewing tube (Hach No. 1730-00) | - 10 |
| | c. Hollow polyethylene stoppers (Hach No. 14480-74) | - 10 |
| 8. | Filtration Apparatus and Supplies | |
| | a. Membrane filters, 0.45 µm, 47 mm diameter (Gelman No. 60173) (package of 100) | - 7 pkg/week |
| | b. Teflon or plastic forceps | - 5 |
| | c. Fisher filtrator - low form (Fisher 09-788) | - 3 |
| | d. Acrylic vacuum chambers (custom made) | - 6 |
| | e. Clean filter holder (Nalgene No. 310-4000) | - 12 |
| | f. Spare rubber stoppers (Fisher No. 09-788-2) | - 6 |
| | g. Vacuum pump with regulator (Millipore No. xx5500000) | - 1 |
| 9. | Hydrolab Model 4041 (spare) | - 1 |
| 10. | Hydrolab Supplies | - 2 |
| | a. Spare probe | - 1 |
| | b. Spare cable (200 m) | - 1 |
| | c. Membrane/KCl kit (high sensitivity) | - 2 |
| | d. Calibration standards | |
| | e. Miscellaneous tools | |
| 11. | Disposable Gloves (talc-free) | |
| 12. | Preservation Supplies | |
| | a. Repipet Jr. (0.1 mL) | - 2 |
| | b. Indicating pH paper (Whatman Type CS No. 2626-990 range 1.8 - 3.8) | - 6 packs/week |
| | c. $HNO_3$ and $H_2SO_4$ (Baker Ultrex grade or Seastar Ultrapure grade) | - 50 mL/week |
| 13. | Frozen Freeze Gel Packs - daily use (reuseable) | - 25/day |
| | - shipping | - 30/40 sample batch |
| 14. | Styrofoam-Lined Shipping Containers | - 4/day |

(continued)

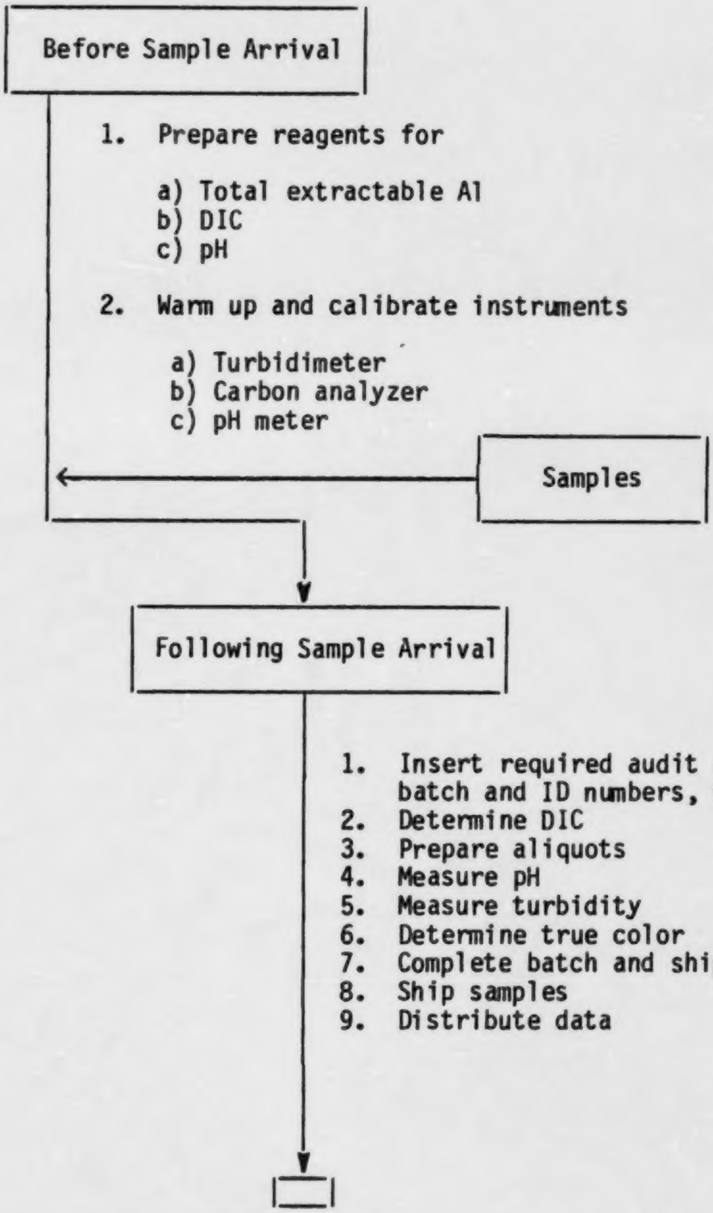
TABLE 2.1. (Continued)

| | | |
|---|---|---|
| 15. | Field Data Forms, Shipping Forms, Batch Forms, etc. | |
| 16. | Buoys (spare) | - 2 |
| 17. | Color Blindness Test Kit | - 1 |
| 18. | DIC Determination Supplies | |
| a. | Dohrman DC-80 carbon analyzer | - 1 |
| b. | 50-mL polypropylene syringes - station use | - 50 |
| | - field use | - 1/sample |
| c. | "Mininert" syringe valves - station use | - 20 |
| | - field use | - 70 |
| d. | Zero-grade nitrogen gas | - 1 cylinder/month |
| e. | Anhydrous $Na_2CO_3$ (ACS Primary Standard Grade) | - 500 g |
| f. | Syringe membrane filters (Gelman Acrodisc 4218, 0.45 µm) | - 1/sample |
| g. | Spare carbon analyzer parts (nuts, ferrules, tubing, etc.) | |
| 19. | Field Station pH Supplies | |
| a. | pH meter (Orion Model 611) | - 2 |
| b. | Orion Ross epoxy body combination pH electrode | - 6 |
| c. | Filling solution for Ross combination pH electrode (pack of 6 bottles) | - 2 |
| d. | pH sample chamber | - 2 |
| e. | Certified 0.100 N $H_2SO_4$ | - 2 L |
| f. | Ringstand (to hold pH apparatus) and clamps | - 2 |
| g. | NBS-traceable pH buffers (pH 4 and 7) | - 2 L of each/ month |
| h. | 50-mL disposable beakers | - 200 |
| 20. | Turbidimeter (Monitek Model 21) | - 1 |
| 21. | Turbidimeter Supplies | - |
| a. | 5-, 10-, 20-, 50-, 100-, 200-NTU standards | - 1 L of each |
| b. | Cuvettes | - 10 |
| 22. | Class 100 Air Filtration Filters | - 6 |
| 23. | Spare Water Treatment Cartridges | - 6 |

(continued)

TABLE 2.1. (Continued)

| | |
|---|---|
| 24. Coolers | - 4 |
| 25. Depth Finder (spare) | - 1 |
| 26. Clean 20-L Cubitainers with Spigots | - 5 |
| 27. Digital Micropipets (5-40 µL, 40-200 µL, 200-1,000 µL, 1,000-5,000 µL) | - 1 of each |
| 28. Micropipet Metal-Free Pipet Tips (in four sizes corresponding to micropipet sizes in item 27) | - 2 cases (1,000 tips/case) of each size |



Before Sample Arrival

1. Prepare reagents for
    - a) Total extractable Al
    - b) DIC
    - c) pH
2. Warm up and calibrate instruments
    - a) Turbidimeter
    - b) Carbon analyzer
    - c) pH meter

Samples

Following Sample Arrival

1. Insert required audit samples, assign batch and ID numbers, start batch form
2. Determine DIC
3. Prepare aliquots
4. Measure pH
5. Measure turbidity
6. Determine true color
7. Complete batch and shipping forms
8. Ship samples
9. Distribute data

Figure 2.1. Flow scheme of daily field station activities.

are shipped to their destinations. These steps are detailed in sections 2.2.2.1 through 2.2.2.4.

2.2.2.1 Sample Identification and Batch Organization--Three types of samples (routine, duplicate, and blank) are collected and delivered to the field station. The sample type is indicated on the sample label (Figure 2.2). The samples collected on a given day are organized into a batch, consisting of 20 to 30 samples, which includes all the routine, duplicate, and blank samples collected on that day as well as audit samples (inserted daily at field station) and split samples (prepared daily by the field station from the routine, duplicate, and blank samples).

After organization, a unique batch ID number is assigned to each batch and is recorded on the labels (and corresponding aliquot labels) of all samples in the batch. Next, an ID number is randomly assigned to each sample as follows:

Routine Samples - Three sample containers are filled at each lake, namely, two syringes (for DIC and pH determination) and a cubitainer. One ID number is assigned to all three containers and is recorded on each container label.

Duplicate and Blank Samples - ID numbers are assigned in the same manner as for the routine samples. (Note: There are no syringe samples for the blank.)

Split Samples - One ID number is assigned and recorded on the cubitainer label of the samples which are split.

Field Audit Samples - One 2-L field audit sample (received each day from a central source) is inserted into each day's batch of samples. The field audit sample is assigned an ID number in the same manner as a routine sample and the number is recorded on the label (Figure 2.3a).

Lab Audit Samples - One lab audit sample (received from a central source) is included in each day's batch. A single lab audit sample consists of a set of seven aliquots. Each aliquot has a temporary label (Figure 2.3b) listing the aliquot number, audit sample code, preservative amount, and shipping date. The lab audit sample is then assigned batch and sample ID numbers in the same manner as for a routine sample. An aliquot label (Figure 2.3c) is attached to each aliquot, and the batch and sample ID numbers are recorded on the label, as are the date and amount of preservative added.

After the batch and sample ID numbers have been assigned and recorded on each sample label, the same information is recorded on Form 2, Batch/QC Field Data. (Figure 2.4). Codes necessary to complete the form are given in Table 2.2.

| | |
|---|---|
| Lake ID<br>____________ | Crew ID<br>____________ |
| Date Sampled<br>____________ | Time Sampled<br>____________ |
| Sample Type (Check One)<br>Routine ______<br>Duplicate ______<br>Blank ______ | |
| Batch ID<br>____________ | Sample ID<br>____________ |

Figure 2.2. Field sample label.

| | |
|---|---|
| FIELD AUDIT SAMPLE | |
| Radian ID No. | |
| Date Shipped | Date Received |
| Code | |
| Batch | ID |

a. Field Audit Sample Label

| | |
|---|---|
| LAB AUDIT SAMPLE | |
| Aliquot No. | |
| Date Shipped | Date Received |
| Code | |
| Preservative Amount | |

b. Lab Audit Sample Label

Aliquot ____________

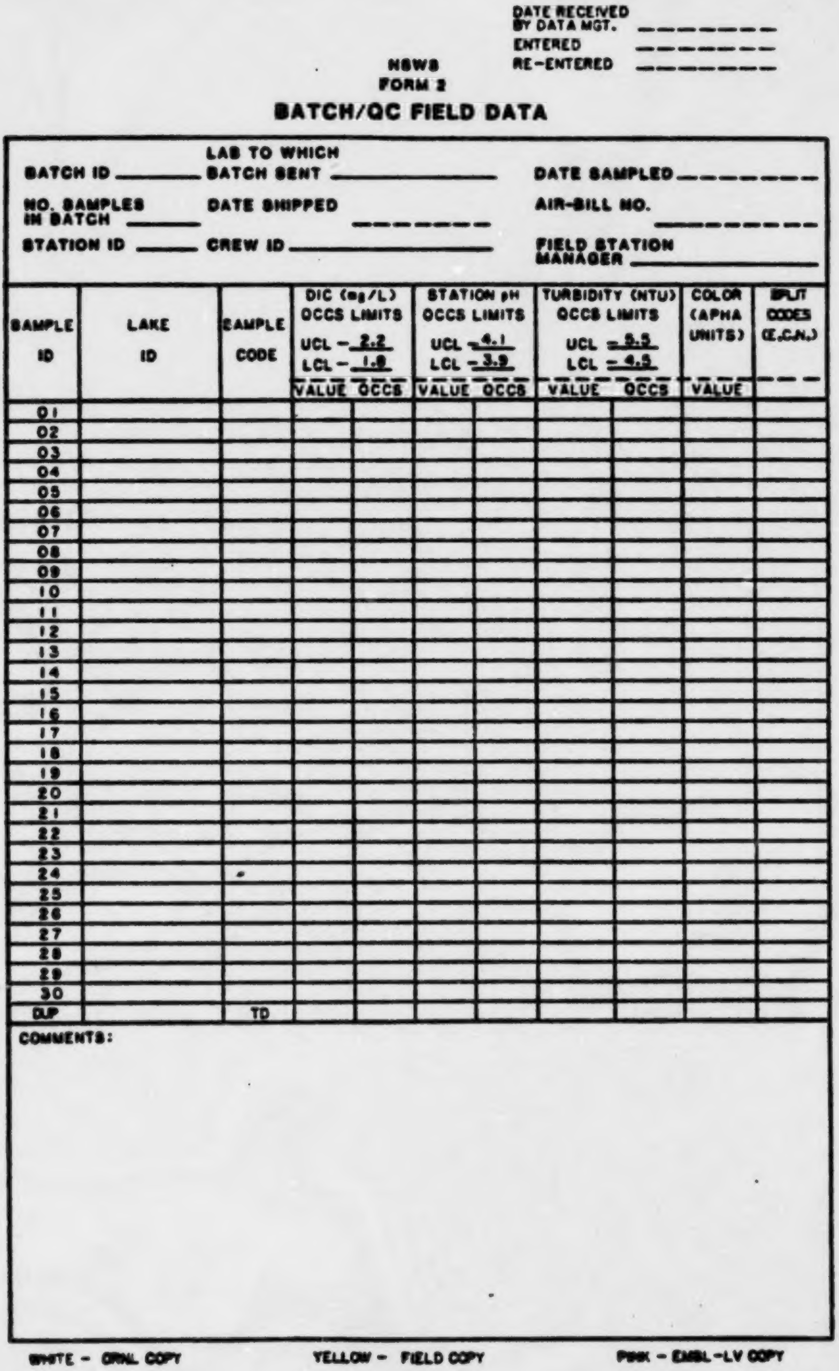
Batch ID ____________
Sample ID ____________
Date Sampled ____________

Preservative ____________
Amount ____________
Parameters ____________

Note: The aliquot no., preservative, and parameters are preprinted on the seven aliquot labels.

c. Aliquot Label

Figure 2.3. Aliquot and Audit Sample Labels.



DATE RECEIVED BY DATA MGT. ________
ENTERED ________
RE-ENTERED ________

NSWS
FORM 2
**BATCH/QC FIELD DATA**

BATCH ID ______
LAB TO WHICH BATCH SENT ______
DATE SAMPLED ________
NO. SAMPLES IN BATCH ______
DATE SHIPPED ________
AIR-BILL NO. ________
STATION ID ______
CREW ID ______
FIELD STATION MANAGER ______

| SAMPLE ID | LAKE ID | SAMPLE CODE | DIC (mg/L) QCCS LIMITS UCL – 2.2 LCL – 1.8 | | STATION pH QCCS LIMITS UCL – 4.1 LCL – 3.9 | | TURBIDITY (NTU) QCCS LIMITS UCL = 5.5 LCL = 4.5 | | COLOR (APHA UNITS) | SPLIT CODES (E,C,N.) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | VALUE | QCCS | VALUE | QCCS | VALUE | QCCS | VALUE | |
| 01 | | | | | | | | | | |
| 02 | | | | | | | | | | |
| 03 | | | | | | | | | | |
| 04 | | | | | | | | | | |
| 05 | | | | | | | | | | |
| 06 | | | | | | | | | | |
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| 27 | | | | | | | | | | |
| 28 | | | | | | | | | | |
| 29 | | | | | | | | | | |
| 30 | | | | | | | | | | |
| DUP | | TD | | | | | | | | |

COMMENTS:

WHITE – ORNL COPY
YELLOW – FIELD COPY
PINK – EMSL-LV COPY

Figure 2.4. NSWS Form 2 - Batch/QC Field Data.

TABLE 2.2. LIST OF SAMPLE CODES

| Sample Type | Code | Description |
|---|---|---|
| Normal | R | Routine Lake Sample |
| | D | Duplicate Lake Sample |
| | B | Field Blank Sample |
| | TD | Field Station (Trailer) Duplicate |
| Audit | F L 1-1 | 1-1 (second digit): Radian ID Number<br>1 (first digit): Concentrate Lot Number<br>L: Concentration Level (L = low, H = high, N = natural)<br>F: Type of Audit Sample (F = field audit sample, L = lab audit sample, P = performance evaluation sample) |
| Split | E | A split sample consists of two sets of aliquots. Each set has the same ID number as assigned in Section 2.2.2, so there is one ID number associated with each split sample. However, for a split sample the letter E (or N or C, depending on where it is shipped) is recorded under the Split Code column on Form 2.<br>Shipping destination of split sample (N = Norwegian lab, C = Canadian lab, E = EPA Corvallis lab) |

NOTE 1: The ID numbers are randomly assigned to all samples in a batch. Furthermore, ID numbers run consecutively from 1 to the number of samples in the batch. Audit samples must not always be assigned the same ID number.

NOTE 2: Field audit samples are processed exactly like routine lake samples. Lab audit samples receive no field treatment other than labeling and shipping.

NOTE 3: After Form 2 is completed, the temporary label on the lab audit sample (seven aliquots) is removed and placed in the lab audit logbook.

2.2.2.2 Determination of DIC, pH, Turbidity, and True Color--These parameters are measured as described in sections 2.3, 2.4, 2.5, and 2.6, respectively.

2.2.2.3 Aliquot and Split Sample Preparation--Seven aliquots are prepared from each sample (routine, duplicate, or blank), each with the same batch and sample ID numbers. The details for preparing each aliquot are provided in section 2.7. The preparation of "split" samples is also described in section 2.7.

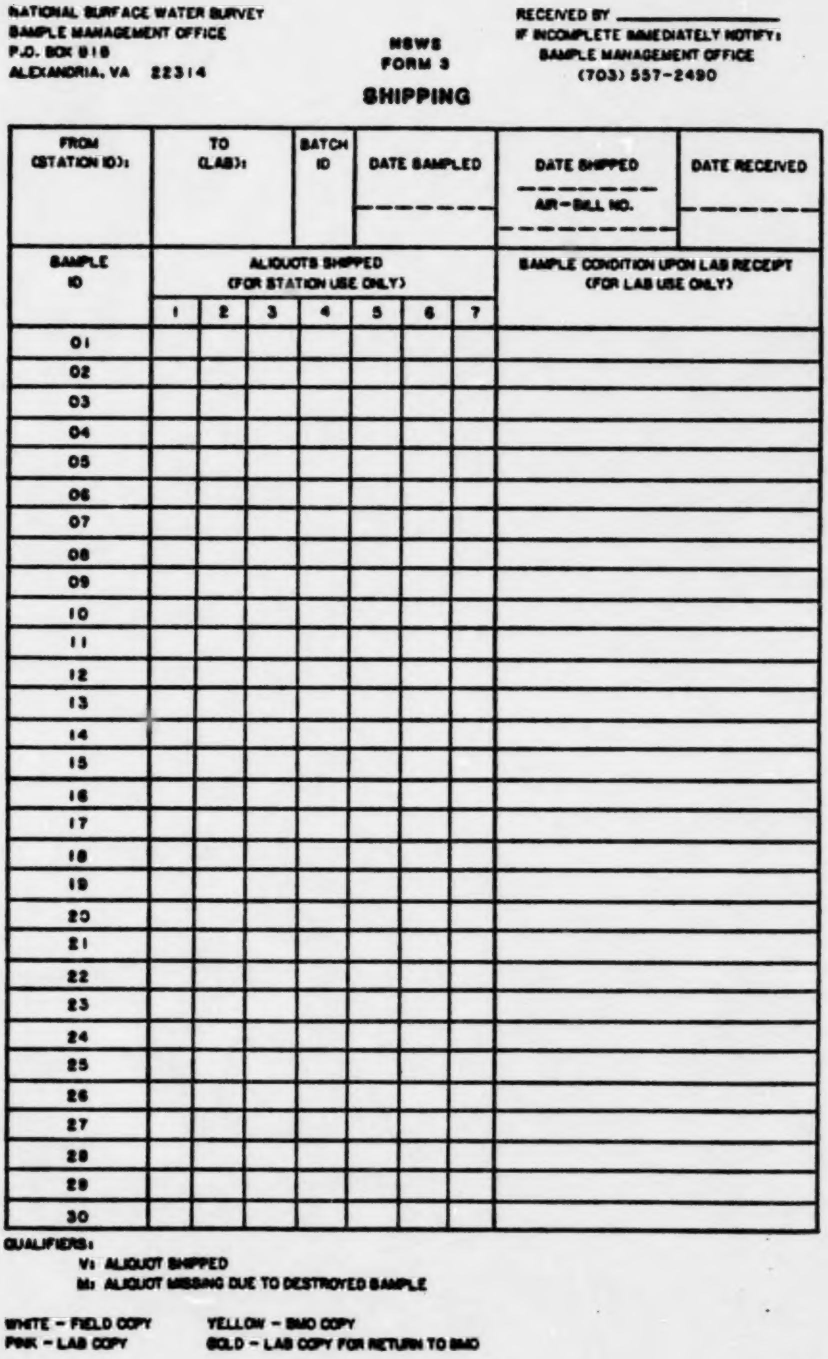
2.2.2.4 Form Completion, Sample Shipment, and Data Distribution--After a batch has been completely processed, the supervisor records all analytical data on Form 2 (Figure 2.4). The coordinator then reviews and signs the form. Next, each aliquot is sealed in a plastic bag and is packed in a Styrofoam-lined shipping container, along with 7 to 10 frozen freeze-gel packs (to maintain aliquots at 4°C). A shipping form (Figure 2.5) is then completed and enclosed with each container and shipped by overnight delivery to its destination. Finally, copies of Forms 1 (a form completed by sampling crew for each sample), 2, and 3 are sent to the locations indicated in Figure 2.6.

## 2.3 Determination of DIC

### 2.3.1 Scope and Application

This method is applicable to the determination of DIC in natural surface waters and is written specifically for the NSWS. DIC is determined in NSWS mobile field laboratories using a Dohrman DC-80 Carbon Analyzer. For this reason, the method has been written assuming that the DC-80 is being used (Xertex - Dohrman Corp., 1984).

The method detection limit (MDL) for DIC determined from replicate analyses of a calibration blank (approximately 0.1 mg/L DIC) is 0.1 mg/L DIC.



NATIONAL SURFACE WATER SURVEY
SAMPLE MANAGEMENT OFFICE
P.O. BOX 818
ALEXANDRIA, VA 22314

NSWS
FORM 3

SHIPPING

RECEIVED BY ____________
IF INCOMPLETE IMMEDIATELY NOTIFY:
SAMPLE MANAGEMENT OFFICE
(703) 557-2490

| FROM (STATION ID): | TO (LAB): | BATCH ID | DATE SAMPLED | DATE SHIPPED<br>AIR-BILL NO. | DATE RECEIVED |
|---|---|---|---|---|---|
| | | | | | |

| SAMPLE ID | ALIQUOTS SHIPPED (FOR STATION USE ONLY) | | | | | | | SAMPLE CONDITION UPON LAB RECEIPT (FOR LAB USE ONLY) |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| 01 | | | | | | | | |
| 02 | | | | | | | | |
| 03 | | | | | | | | |
| 04 | | | | | | | | |
| 05 | | | | | | | | |
| 06 | | | | | | | | |
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| 28 | | | | | | | | |
| 29 | | | | | | | | |
| 30 | | | | | | | | |

QUALIFIERS:
V: ALIQUOT SHIPPED
M: ALIQUOT MISSING DUE TO DESTROYED SAMPLE

WHITE – FIELD COPY    YELLOW – SMO COPY
PINK – LAB COPY    GOLD – LAB COPY FOR RETURN TO SMO

Figure 2.5. NSWS Form 3 - Shipping.

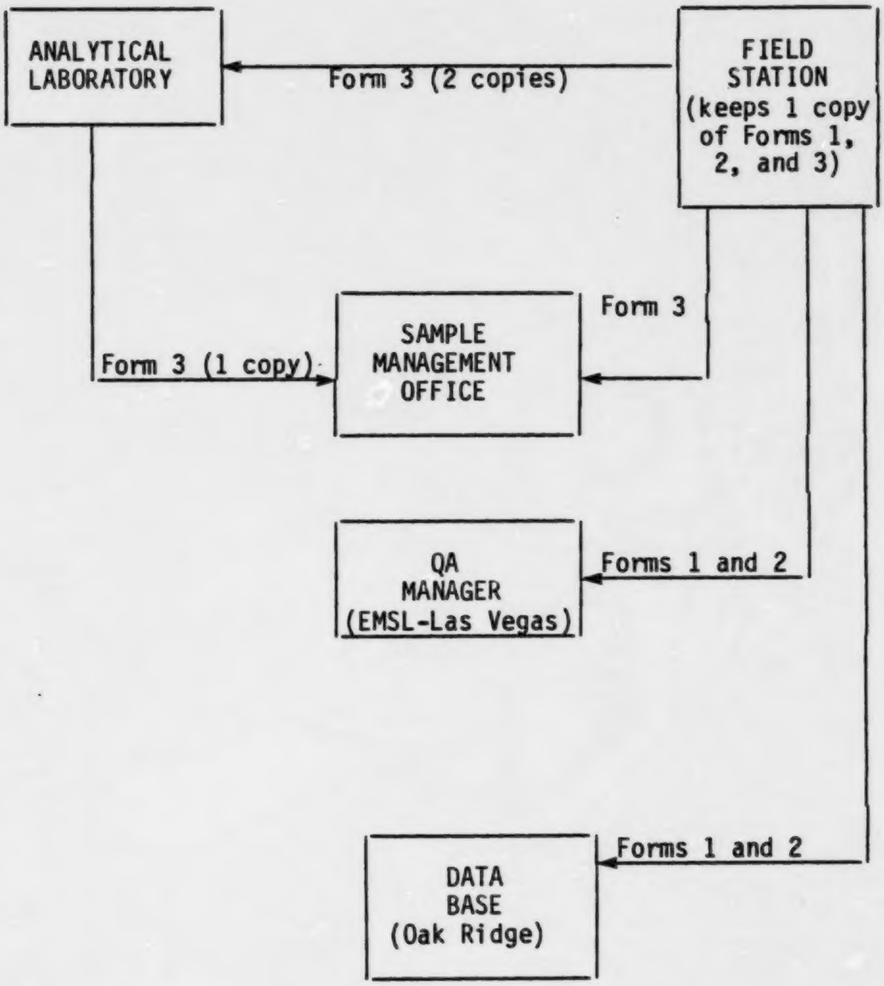

ANALYTICAL LABORATORY
Form 3 (2 copies)
FIELD STATION (keeps 1 copy of Forms 1, 2, and 3)
Form 3
Form 3 (1 copy)
SAMPLE MANAGEMENT OFFICE
QA MANAGER (EMSL-Las Vegas)
Forms 1 and 2
Forms 1 and 2
DATA BASE (Oak Ridge)

Figure 2.6. Data flow scheme.

A 1.00-mL sample volume was used to determine the MDL. The applicable analyte concentration range is 0.1 to 50 mg/L DIC.

### 2.3.2 Summary of Method

Samples for DIC determination are collected and sealed at the lake sites in syringes. At the field station, a syringe filter is attached to the syringe and sample is filtered into the sample loop of the DC-80. The sample is subsequently injected into a reaction chamber containing 5 percent phosphoric acid. The carbonates (DIC) in the sample react with the acid to form $CO_2$, which is sparged from the reaction chamber with a nitrogen gas carrier stream. The $CO_2$ in the carrier stream is then detected and quantified (in terms of DIC) by an infrared (IR) $CO_2$ analyzer.

### 2.3.3 Interferences

No interferences are known.

### 2.3.4 Safety

The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Protective clothing (lab coat and gloves) and safety glasses must be used when handling concentrated phosphoric acid.

The nitrogen cylinder must be secured in an upright position. The line pressure must be kept below 40 psi.

### 2.3.5 Apparatus and Equipment

- Dohrmann DC-80 Carbon Analyzer equipped with High Sensitivity Sampler (1.00-mL loop).
- Reagent bottles for DIC standards (equipped with three-valve cap to permit storage under a $CO_2$-free atmosphere, Rainin No. 45-3200).
- 0.45-µm syringe filters.
- 60-mL plastic syringes.
- Luer-Lok syringe valves.

### 2.3.6 Reagents and Consumable Materials

- Nitrogen Gas (99.9 percent)--$CO_2$-free.
- Phosphoric Acid (5 percent v/v)--Carefully add 50 mL concentrated

phosphoric acid ($H_3PO_4$, sp gr 1.71) to 500 mL water. Mix well and dilute to 1,000 mL with water.

- Stock DIC Quality Control Sample Solution--Weekly, open a fresh ampule of anhydrous, primary standard grade sodium carbonate ($Na_2CO_3$) and dissolve 8.825 g in water, then dilute to 1.000 L. Store at 4°C in a special reagent bottle under a $CO_2$-free atmosphere.

- Stock DIC Calibration Standard Solution--Biweekly, open a fresh ampule of anhydrous, primary standard grade $Na_2CO_3$ and dissolve 8.825 g in water, then dilute to 1.000 L. Store at 4°C in a special reagent bottle under a $CO_2$-free atmosphere.

- Water--Water used in all preparations must conform to ASTM specifications for Type I water (ASTM, 1984). Such water is obtained from the Millipore Milli-Q water system.

### 2.3.7 Sample Collection, Preservation, and Storage

Samples are collected and sealed in 60-mL plastic syringes. They are stored at 4°C until use.

### 2.3.8 Calibration and Standardization

Step 1--Set up and operate the DC-80 according to the manufacturer's instructions.

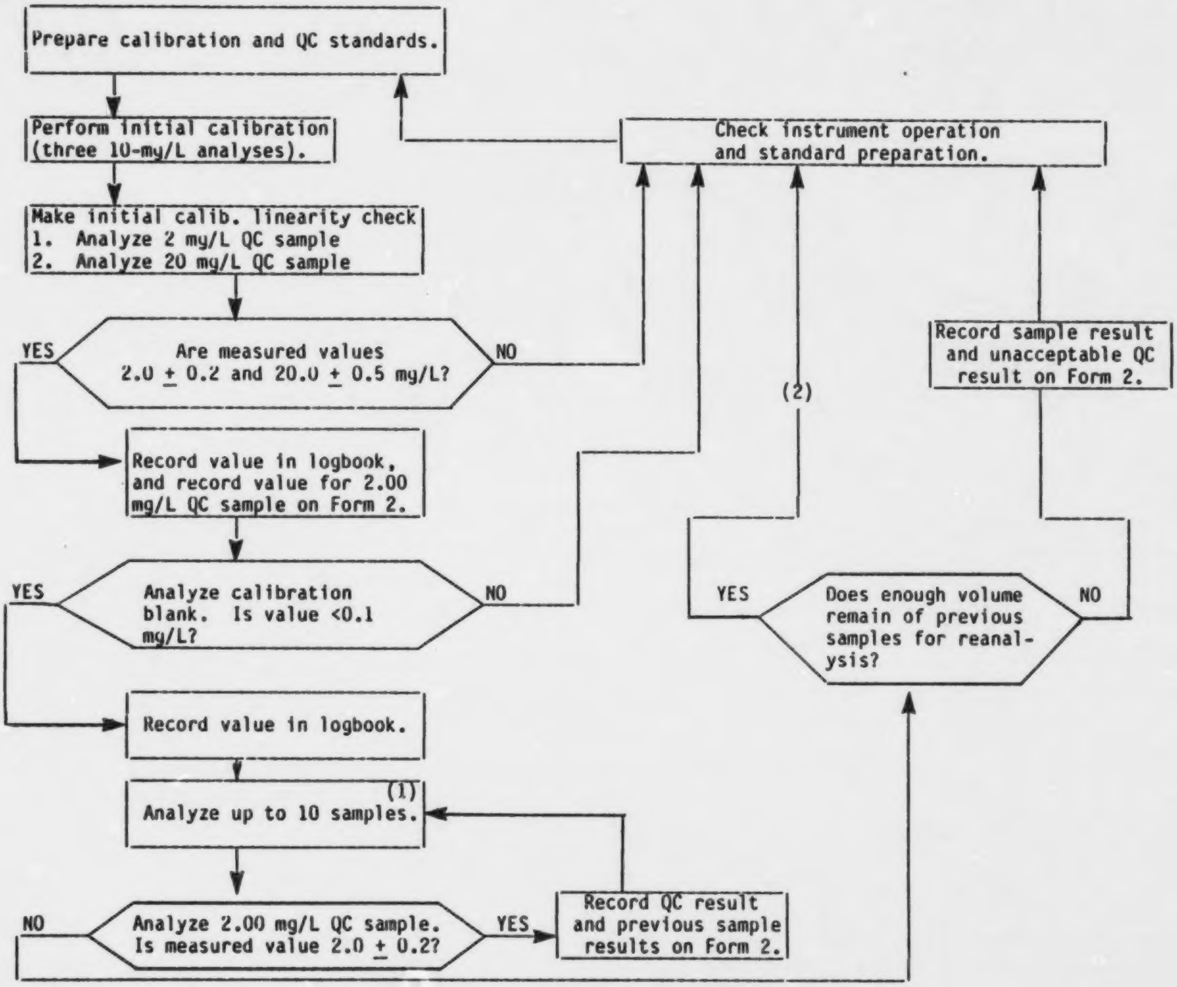
Step 2--Prepare the calibration standard (10.00 mg/L DIC) daily by diluting 5.000 mL of the stock DIC calibration standard to 500.00 mL with fresh water. Store in a special reagent bottle under a $CO_2$-free atmosphere.

Step 3--Erase previous calibration. Load the sample loop with the 10.00-mg/L DIC calibration standard by flushing with 7 to 10 mL solution. Inject and start the analysis. When the analysis is complete, repeat the process twice more.

Step 4--Calibrate the analyzer by pushing the calibrate button. This completes the calibration. Sample results are output directly in mg/L DIC.

### 2.3.9 Quality Control

QC procedures are outlined in Figure 2.7 and are described in sections 2.3.9.1 through 2.3.9.5.


Prepare calibration and QC standards.
Perform initial calibration (three 10-mg/L analyses).
Make initial calib. linearity check
1. Analyze 2 mg/L QC sample
2. Analyze 20 mg/L QC sample
YES
Are measured values 2.0 ± 0.2 and 20.0 ± 0.5 mg/L?
NO
Record value in logbook, and record value for 2.00 mg/L QC sample on Form 2.
YES
Analyze calibration blank. Is value <0.1 mg/L?
NO
Record value in logbook.
Analyze up to 10 samples. (1)
NO
Analyze 2.00 mg/L QC sample. Is measured value 2.0 ± 0.2?
YES
Record QC result and previous sample results on Form 2.
Check instrument operation and standard preparation.
(2)
Record sample result and unacceptable QC result on Form 2.
YES
Does enough volume remain of previous samples for reanalysis?
NO

(1) Analyze one sample per batch in duplicate.
(2) Reanalyze samples associated with unacceptable QC result.

Figure 2.7. Flow scheme for DIC determinations.

2.3.9.1 Initial Calibration Verification and Linearity Check--Immediately after calibration, analyze two QC samples to ensure the calibration validity and linearity.

Daily, prepare a 2.00-mg/L and a 20.00-mg/L DIC QC sample by diluting 1.000 and 10.00 mL of the stock DIC QC sample, respectively, to 500.00 mL with fresh water. Store each DIC QC sample in a special reagent bottle under a $CO_2$-free atmosphere.

Analyze the QC samples. The results must be 2.0 ± 0.2 and 20.0 ± 0.5 mg/L DIC. If the results do not fall within these ranges, a problem exists in the calibration, standard preparation, or QC sample preparation. The problem must be resolved prior to sample analysis, and the QC samples must be reanalyzed. Acceptable results must be obtained before continuing.

2.3.9.2 Continuing Calibration Verification--To check for calibration drift, analyze the 2.00-mg/L DIC QC sample after every 10 samples and after the last sample. The measured value must be 2.0 ± 0.2 mg/L DIC. If it is not, repeat the calibration and reanalyze all samples analyzed since the last acceptably analyzed QC sample.

2.3.9.3 Calibration Blank Analysis--After the initial calibration, analyze a fresh calibration blank. It must contain less than 0.1 mg/L DIC. If it does not, check the water system and repeat the calibration procedure (including preparation of standards).

2.3.9.4 Duplicate Analysis--To determine the analytical precision, analyze one sample per batch in duplicate.

2.3.9.5 Detection Limit Determination--Determine the detection limit by analyzing 20 blank samples. The detection limit is defined as three times the standard deviation.

2.3.10 Procedure

Step 1--Check that the DC-80 is equilibrated and a stable baseline has been achieved.

Step 2--Prepare calibration standard and calibrate the analyzer.

Step 3--Perform the necessary QC analyses. Proceed with sample analysis if acceptable results are obtained.

Step 4--Place a syringe valve on the sample syringe and filter 7 to 10 mL of sample directly into the sample loop. Inject the sample and start the analysis. Discard the syringe filter after a single use.

Step 5--Thirty seconds after injection, switch the valve to the load position and load the next sample. The analysis time for a single sample is 3 to 4 minutes.

Step 6--At the end of the day, rinse the sample loop with water. Keep the power to the IR analyzer on at all times.

### 2.3.11 Calculations

No calculations are necessary. Sample results are output on the printer directly in mg/L DIC.

### 2.3.12 Reporting

Record the batch and sample ID numbers directly on the printer output. Similarly identify QC samples. Attach the printout to the logbook. Record the sample and QC data on Form 2.

## 2.4 Determination of pH

### 2.4.1 Scope and Application

This method is applicable to the determination of pH in surface waters of low ionic strength and is written specifically for the NSWS. The pH is determined in the field stations using an Orion Model 611 pH meter and an Orion Ross combination pH electrode. As a result, the method has been written assuming that the Orion meter and electrode are used (Orion, 1983).

The applicable pH range is 3 to 11.

### 2.4.2 Summary of Method

Samples for pH determination are collected and sealed in syringes at the lake site. At the field station, pH is measured in a closed system to prevent atmospheric exposure. The measurement is performed by attaching the sample syringe to the pH sample chamber (Figures 2.8 and 2.9), injecting sample, and determining pH using a pH meter and electrode.

### 2.4.3 Interferences

No interferences are known.

### 2.4.4 Safety

The calibration standards, sample types, and reagents used in this

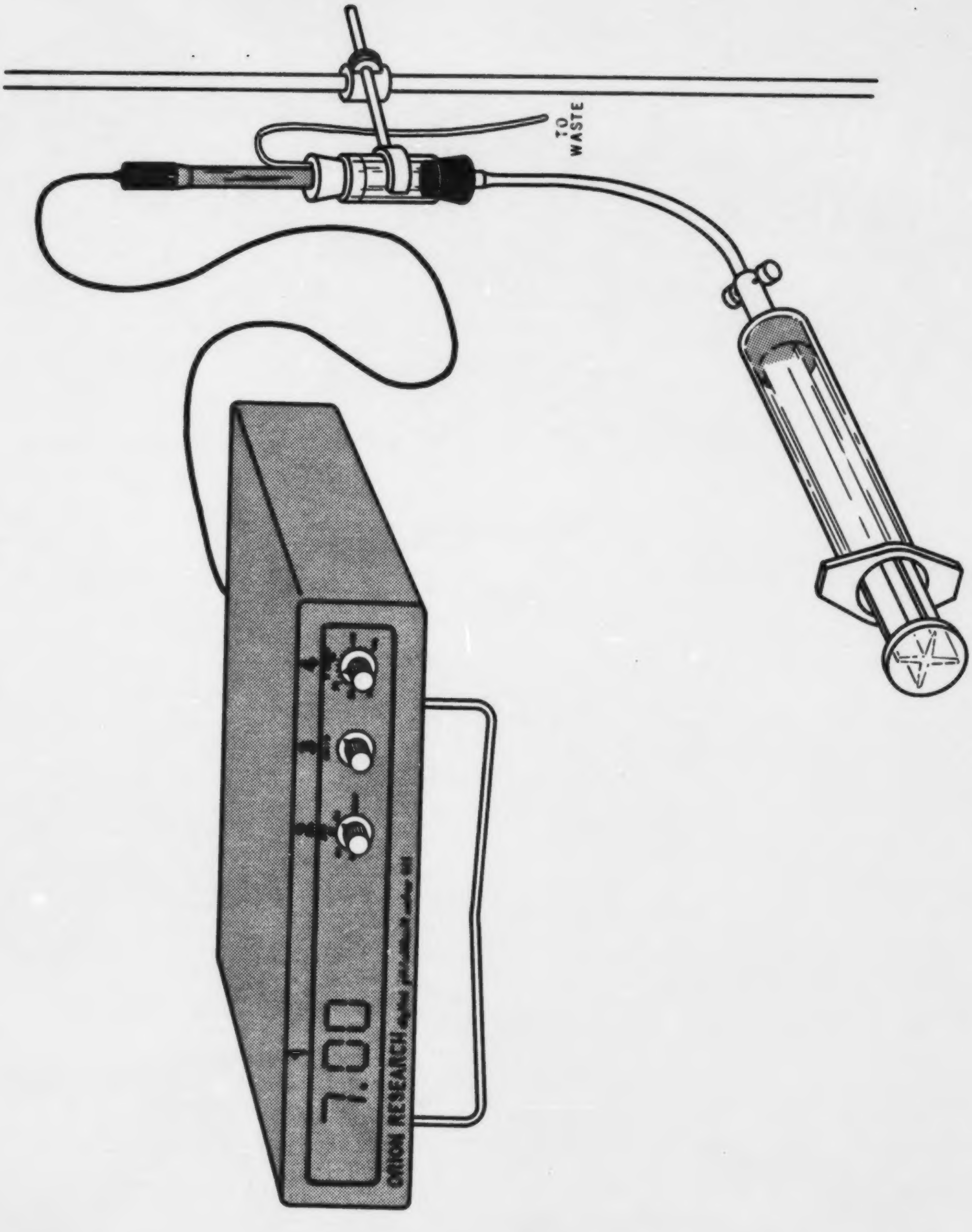

TO WASTE
ORION RESEARCH
7.00

Figure 2.8. Schematic of pH measurement system.

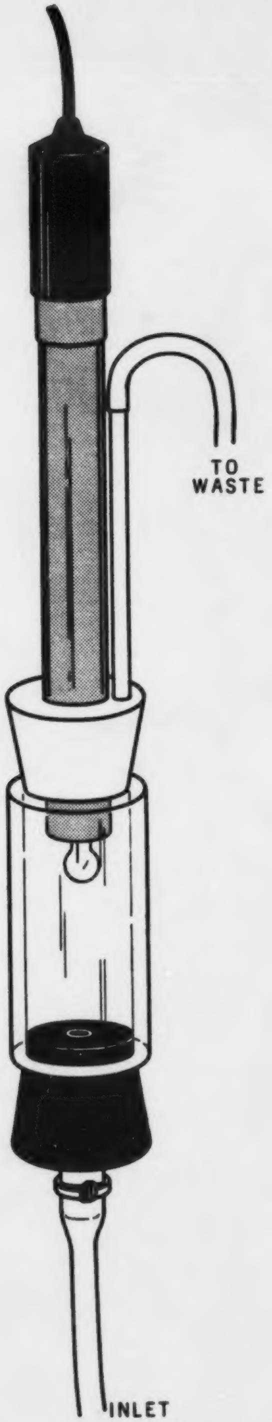

TO
WASTE
INLET

Figure 2.9. pH sample chamber.

method pose no hazard to the analyst. Protective clothing (lab coat and gloves) and safety glasses must be used when handling sulfuric acid.

### 2.4.5 Apparatus and Equipment

- Orion Model 611 pH meter
- Orion Ross combination pH electrode
- pH sample chamber
- 60-mL plastic syringes
- Luer-Lok syringe valves

### 2.4.6 Reagents and Consumable Materials

- pH Calibration Buffers (pH 4 and 7)--Commercially available pH calibration buffers (NBS-traceable) at pH values of 4 and 7.
- Potassium Chloride (3 M)--Dissolve 75 g KCl in 1 L of water.
- Stock pH Quality Control Sample Solution (0.100N $H_2SO_4$)--Commercially available certified standard sulfuric acid at a concentration of 0.100N.
- Water--Water used in all preparations must conform to ASTM specifications for Type I water (ASTM, 1984). It is obtained from the Millipore Milli-Q water system.

### 2.4.7 Sample Collection, Preservation, and Storage

Samples are collected and sealed in 60-mL plastic syringes. They are stored at 4°C until used.

### 2.4.8 Calibration and Standardization

Weekly, calibrate the temperature function of the pH meter and electrode using a two-point calibration (4°C and room temperature) following the manufacturer's instructions.

Daily, calibrate the pH function of the pH meter and electrode using a two-point calibration (pH 7 and 4) following the manufacturer's instructions. Generally, the calibration involves setting the meter calibration control while measuring pH 7 buffer and the slope control while measuring pH 4 buffer. After calibration, the calibration accuracy is checked as described in the following procedure:

Step 1--Copiously rinse the electrode with water. Immerse in 20 mL pH 7 buffer and stir for 30 to 60 seconds. Discard and replace with an additional 40 mL pH 7 buffer. While the solution is gently stirred, measure and record the pH.

Step 2--Repeat step 1 using the pH 4 buffer.

Step 3--Compare the pH values obtained for the pH 7 and 4 buffers in steps 1 and 2 to the certified values of the buffers. If either observed value differs from the certified value by more than ±0.02 pH units, repeat the electrode calibration. If acceptable results cannot be obtained, replace the electrode.

### 2.4.9 Quality Control

QC procedures are outlined in Figure 2.10 and are described in sections 2.4.9.1 through 2.4.9.4.

2.4.9.1 pH QC Check Sample--Daily, prepare a pH QC check sample (pH QCCS) by diluting 1.000 mL of the 0.100N $H_2SO_4$ to 1.000 L with water.

2.4.9.2 Initial pH QC Check--Immediately after calibration, analyze the pH QCCS using the procedure described in section 2.4.8.3. The observed pH must be 4.0 ± 0.1 pH unit. If it is not, repeat the calibration process (section 2.4.8), then repeat the measurement on a fresh pH QCCS. If an acceptable result is still not obtained, consult the manufacturer's troubleshooting guide for the meter and electrode. Lake samples must not be analyzed until an acceptable value for the pH QCCS is obtained.

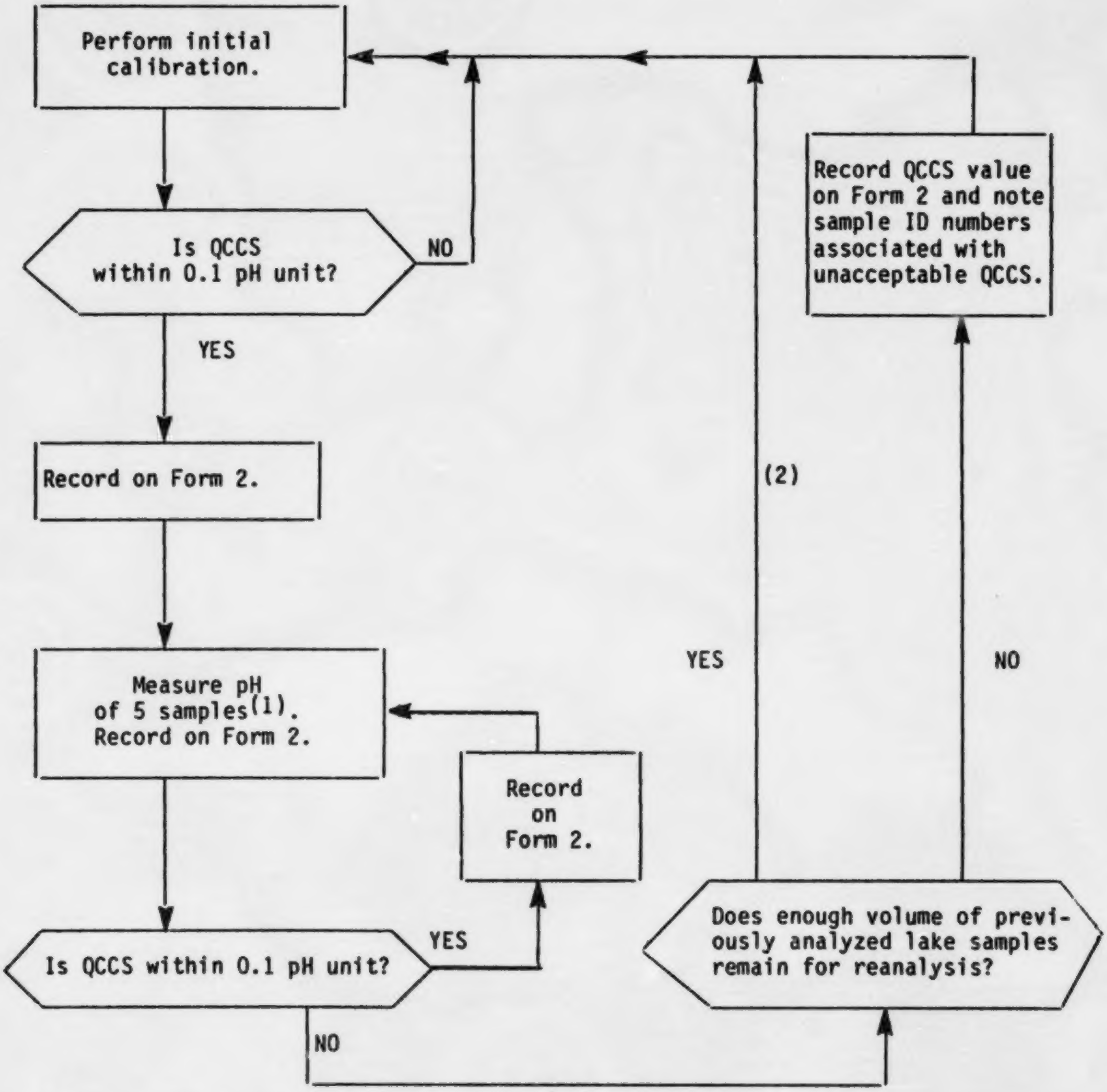
2.4.9.3 Continuing pH QC Check--In order to check for calibration drift, the pH QCCS sample is analyzed after every five samples and after the last sample. The measured valve must be 4.0 ± 0.1 pH unit. If it is not, recalibrate the electrode and meter and reanalyze all samples analyzed since the last acceptably analyzed pH QCCS.

2.4.9.4 Duplicate Analysis--To determine the analytical precision, analyze one sample per batch in duplicate.

### 2.4.10 Procedure

Step 1--Calibrate the pH meter and electrode.

Step 2--Perform the required QC analysis. Proceed with sample analyses if acceptable results are obtained.


Perform initial calibration.
Is QCCS within 0.1 pH unit?
NO
YES
Record on Form 2.
Measure pH of 5 samples(1). Record on Form 2.
Record on Form 2.
Is QCCS within 0.1 pH unit?
YES
NO
Does enough volume of previously analyzed lake samples remain for reanalysis?
YES
(2)
NO
Record QCCS value on Form 2 and note sample ID numbers associated with unacceptable QCCS.

(1) Measure 1 sample per batch in duplicate (same syringe).
(2) Previous samples must be reanalyzed after unacceptable QCCS is obtained.

Figure 2.10. Flow scheme for pH determinations.

Step 3--Clamp a pH sample chamber to a ringstand. Rinse thoroughly with water.

Step 4--Equilibrate the sample syringes to room temperature.

Step 5--Attach a sample syringe to the sample chamber. Fill the chamber with sample. Rinse the electrode in the top of the chamber for 15 to 30 seconds. Drain the chamber and repeat. Refill the chamber with sample and loosely insert the electrode. Flush with 5 to 10 mL sample to expel air bubbles, then lightly seal the chamber. Measure and record the sample pH and temperature. Monitor the pH reading. Record the reading when it stabilizes (± 0.02 pH unit/minute, usually about 1 to 5 minutes). Slowly inject 5 mL sample over a 60-second period. Measure the pH and record when stable. Repeat the 5-mL injections until successive pH readings are within 0.03 pH units.

Step 6--Rinse the sample chamber and electrode copiously with water between samples.

Step 7--At the end of the day, store the electrode in 3 M KCl.

### 2.4.11 Calculations

No calculations are required.

### 2.4.12 Reporting

Record the raw data in the pH logbook, and record the final sample pH value on Form 2. Also record the initial and continuing QC results on Form 2.

## 2.5 Determination of Turbidity

### 2.5.1 Scope and Application

This method is applicable to the determination of turbidity in natural surface waters and is written specifically for the NSWS. Turbidity is determined in the field stations using a Monitek Model 21 nephelometer. As a result, the method has been written assuming that the Monitek nephelometer is used (Monitek, 1977).

The applicable turbidity range is 0 to 200 NTUs.

### 2.5.2 Summary of Method

Samples are collected at the lake site in Cubitainers. At the field station the sample turbidity is measured directly in NTU's, using a calibrated nephelometer.

### 2.5.3 Interferences

Air bubbles in the sample cuvette interfere with the determination and cause a positive bias.

### 2.5.4 Safety

The calibration standards and sample types pose no hazard to the analyst.

### 2.5.5 Apparatus and Equipment

- Monitek Model 21 nephelometer
- Sample cuvettes

### 2.5.6 Reagents and Consumable Materials

- Turbidity Calibration Standard (10 NTU)--Commercially available certified turbidity standard.
- Turbidity Quality Control Samples (1.7, 5, 20, 50, 100, and 200 NTU)--Commercially available certified turbidity standards.

### 2.5.7 Sample Collection, Preservation, and Storage

Lake samples are collected in plastic Cubitainers and are stored at 4°C until use.

### 2.5.8 Calibration and Standardization

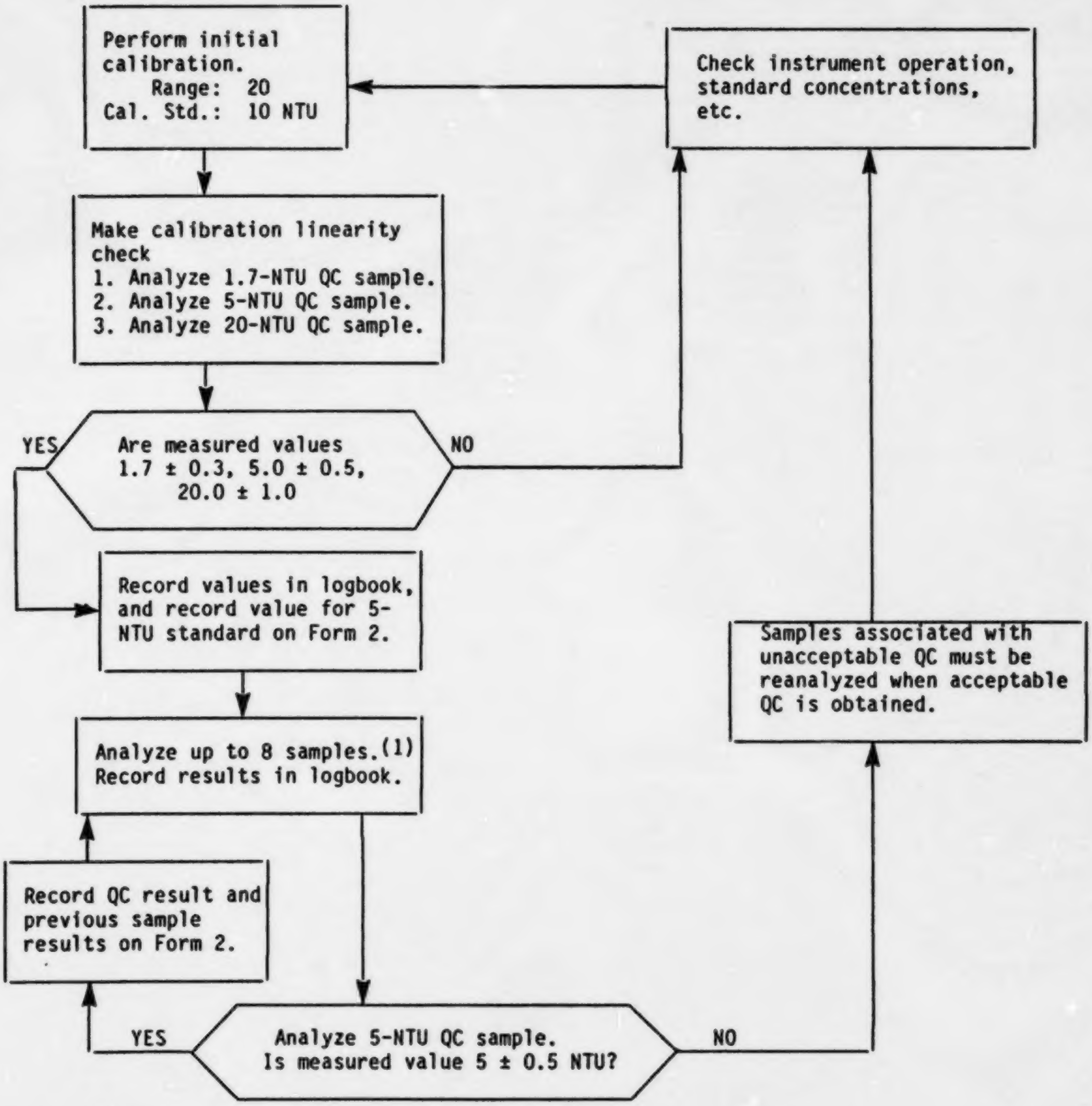
Step 1--Turn on the nephelometer power and lamp. Allow to warm up for 15 to 30 minutes.

Step 2--Set the nephelometer range switch to 20. Zero the instrument with the zero knob.

Step 3--Place the 10.0-NTU calibration standard in the instrument. Calibrate by setting the reading to 10.0 with the calibrate knob.

### 2.5.9 Quality Control

QC procedures are outlined in Figure 2.11 and are described in sections 2.5.9.1 through 2.5.9.3.


Perform initial calibration.
Range: 20
Cal. Std.: 10 NTU
Check instrument operation, standard concentrations, etc.
Make calibration linearity check
1. Analyze 1.7-NTU QC sample.
2. Analyze 5-NTU QC sample.
3. Analyze 20-NTU QC sample.
YES
Are measured values 1.7 ± 0.3, 5.0 ± 0.5, 20.0 ± 1.0
NO
Record values in logbook, and record value for 5-NTU standard on Form 2.
Samples associated with unacceptable QC must be reanalyzed when acceptable QC is obtained.
Analyze up to 8 samples.(1) Record results in logbook.
Record QC result and previous sample results on Form 2.
YES
Analyze 5-NTU QC sample. Is measured value 5 ± 0.5 NTU?
NO

(1)Analyze one sample per batch in duplicate.

Figure 2.11. Flow scheme for turbidity determinations.

2.5.9.1 Initial Calibration Verification and Linearity Check--Immediately after calibration, analyze the 1.7-, 5.0-, and 20.0-NTU QC samples to ensure the calibration validity and linearity. The measured values must be 1.7 ± 0.3, 5.0 ± 0.5, and 20.0 ± 1.0. If the measured values are unacceptable, the calibration must be repeated. Ensure that the instrument is warmed up and that the cuvettes are clean. Acceptable results must be obtained prior to sample analysis.

2.5.9.2 Continuing Calibration Check--After every eight samples and after the last sample reanalyze the 5.0-NTU QC sample. The measured value must be 5.0 ± 0.5 NTU. If it is not, recalibrate the instrument and reanalyze all samples analyzed since the last acceptably analyzed QC sample.

2.5.9.3 Duplicate Analysis--In order to determine the analytical precision, analyze one sample per batch in duplicate.

### 2.5.10 Procedure

Step 1--Warm up the nephelometer.

Step 2--Calibrate the nephelometer.

Step 3--Analyze the QC samples. Proceed with the sample analysis if acceptable results are obtained.

Step 4--Allow the sample Cubitainer to reach room temperature. Gently swirl sample Cubitainers to mix and distribute any particles which may have settled out during sample transport. Care must be taken to avoid agitation-induced air bubbles, which interfere with the measurement. Rinse the nephelometer cuvette with two 5-mL portions of sample, then fill (approximately 25 mL sample). Wipe the cuvette with a Kimwipe, insert the cuvette into the nephelometer, and measure the turbidity on range 20. (Note: Fingerprints, bubbles, smudges, etc., must be avoided because they will affect the accuracy of the system.) The turbidity of a sample is not expected to exceed 20 NTU; however, if this occurs, the sample must be analyzed on range 200. In this case, a QC sample with a turbidity greater than the sample must be analyzed (50-, 100-, or 200-NTU QC samples are available). Acceptable results for the QC samples are 50 ± 2.5, 100 ± 5, and 200 ± 10, respectively. If an acceptable QC value is not obtained, the turbidimeter must be recalibrated on range 200 using a 100-NTU QC standard, and the sample must be reanalyzed. If the sample turbidity exceeds 200 NTU, the sample must be diluted 1:10 with filtered sample and must be reanalyzed on range 200 as stated above. The turbidity of the original sample is calculated by multiplying the turbidity of the dilute sample by the dilution factor.

Step 5--Rinse cuvette thoroughly with water between samples.

### 2.5.11 Calculations

No calculations are required.

### 2.5.12 Reporting

Record the sample and QC data in the turbidity logbook and on Form 2. Report only the QC data for the 5.0-NTU QC sample on Form 2.

## 2.6 Determination of True Color

### 2.6.1 Scope and Application

This method is applicable to the determination of true color in natural surface waters and is written specifically for the NSWS. True color is determined in the field station using a Hach Color Determination Kit. As a result, the method has been written assuming that the Hach Color Determination Kit is used.

The applicable color range is 0 to 200 APHA platinum-cobalt color units (PCUs) (APHA, 1985; U.S. EPA, 1983).

### 2.6.2 Summary of Method

Samples are collected at the lake site in Cubitainers. At the field station, the true color is determined after centrifuging a sample and comparing its color to APHA color standards.

### 2.6.3 Interferences

No interferences are known.

### 2.6.4 Safety

The sample types pose no hazard to the analyst.

### 2.6.5 Apparatus and Equipment

- Hach Model CO-1 Color Determination Kit
- Sample cuvettes

### 2.6.6 Reagents and Consumable Materials

- Water--Water used to rinse cuvettes must conform to ASTM specifications for Type I water (ASTM, 1984). It is obtained from the Millipore Milli-Q water system.

### 2.6.7 Sample Collection, Preservation, and Storage

Lake samples are collected in plastic Cubitainers and stored at 4°C until use.

### 2.6.8 Calibration and Standardization

The color kit contains permanent color standards. No calibration is necessary.

### 2.6.9 Quality Control

Duplicate Analysis--To determine the analytical precision, analyze one sample per batch in duplicate.

### 2.6.10 Procedure

Step 1--Allow the samples to reach room temperature.

Step 2--Centrifuge a 50-mL sample to remove turbidity. Rinse a sample cuvette with three 5-mL portions of centrifuged sample. Fill the cuvette with sample, and cap it. Determine the color using the color kit following the manufacturer's instructions.

Step 3--Rinse the sample cuvette thoroughly with water between samples.

### 2.6.11 Calculations

No calculations are necessary.

### 2.6.12 Reporting

Record the sample data in the color logbook and on Form 2.

## 2.7 Aliquot and Split Sample Preparation

### 2.7.1 Summary

Lake samples are collected in 4-L Cubitainers. From each sample, seven aliquots are prepared. Each is processed in a different manner according to which analytes will be determined in the aliquot.

In addition to the seven aliquots, split samples are also prepared from some lake samples. Split samples are similar to the aliquots but are sent to noncontract laboratories (i.e., laboratories not under contract to perform the NSWS analyses) for the purposes of international cooperation and exploratory analyses.

A brief description of the seven aliquots is given in Table 2.3 and of the split samples in Table 2.4.

### 2.7.2 Safety

The sample types and most reagents used in preparing aliquots pose no hazard to the analyst. Protective clothing (lab coat and gloves) and safety glasses must be used when handling concentrated sulfuric, nitric, hydrochloric, and glacial acetic acids and concentrated ammonium hydroxide. The use of hydrochloric and acetic acids and of ammonium hydroxide should be restricted to the hood.

MIBK is a highly flammable organic solvent and must be kept away from ignition sources. Also, MIBK vapor is irritating to the eyes, nose, and throat. Exposure to the vapor may cause temporary irritation. Liquid MIBK is also an irritant. If spilled on skin or in eyes, wash affected area thoroughly with water until irritation stops. The use of MIBK should be restricted to the hood. If it must be used outside of the hood, organic vapor masks should be worn.

### 2.7.3 Apparatus and Equipment

Filtration Apparatus--Includes filter holder, vacuum chamber, and vacuum pumps.

### 2.7.4 Reagents and Consumable Materials

- Ammonium Hydroxide (1 M)--Carefully add 20 mL concentrated ammonium hydroxide ($NH_4OH$, 5 M, Baker Instra-Analyzed grade or equivalent) to 80 mL water, then dilute to 100 mL.

- Hydrochloric Acid (2.5 M)--Carefully add 208 mL concentrated hydrochloric acid (HCl, 12 M, Baker Instra-Analyzed grade or equivalent) to 500 mL water, then dilute to 1.0 L.

- 8-hydroxyquinoline Solution (10 g/L)--Dissolve 5 g 8-hydroxyquinoline (99 percent plus purity) in 12.5 mL glacial acetic acid (HOAc, Baker Instra-Analyzed grade or equivalent), then dilute to 500 mL with water.

- 8-hydroxyquinoline/Sodium Acetate Reagent (HOx Reagent)--Prepare daily by mixing in order, 30 mL 1.0 M NaOAc, 150 mL water, and 30 mL 8-hydroxyquinoline solution.

TABLE 2.3. ALIQUOT DESCRIPTIONS

| Aliquot | Container Description | Description |
|---|---|---|
| 1 | 250 mL<br>(acid-washed) | Filtered sample acidified with $HNO_3$ to a pH <2 |
| 2 | 10 mL<br>(acid-washed) | MIBK-Hydroxyquinoline extract |
| 3 | 250 mL<br>(not acid-washed) | Filtered sample |
| 4 | 125 mL<br>(acid-washed) | Filtered sample acidified with $H_2SO_4$ to a pH <2 |
| 5 | 500 mL<br>(not acid-washed) | Raw unfiltered sample |
| 6 | 125 mL<br>(acid-washed) | Unfiltered sample acidified with $H_2SO_4$ to a pH <2 |
| 7 | 125 mL<br>(acid-washed) | Unfiltered sample acidified with $HNO_3$ to a pH <2 |

TABLE 2.4. SPLIT SAMPLE DESCRIPTIONS

| Split | Container Description | Number | Descriptions |
|---|---|---|---|
| EPA-Corvallis | 250 mL (acid-washed) | All samples[a] | Filtered sample acidified with $HNO_3$ to a pH <2 |
| Norwegian[b] | 500 mL (not acid-washed) | 90 | Raw unfiltered sample |
| Canadian[b] | 250 mL[c] (not acid-washed) | 115 | Raw unfiltered sample |
|  | 250 mL[c] (acid-washed) | 115 | Raw unfiltered sample acidified with $HNO_3$ to pH <2 |
|  | 250 mL[d] (not acid-washed) | 115 | Raw unfiltered sample |
|  | 125 mL[d] (not acid-washed) | 115 | Raw unfiltered sample |

[a] Except when there is insufficient sample due to other splits.
[b] Sample to be taken in the Northeast.
[c] Sent to Ontario Ministry of the Environment, Rexdale, Ontario, Canada.
[d] Sent to Canada Center for Inland Waters, Burlington, Ontario, Canada.

- $NH_4^+/NH_3$ Buffer Solution (pH 8.3)--Adjust the pH of 21 mL concentrated $NH_4OH$ (5 M, Baker Instra-Analyzed grade or equivalent) to 8.3 with 2.5 M HCl (test the pH with indicating pH paper), then add an additional 32 mL of the $NH_4OH$. If the total volume is less than 100 mL, dilute to 100 mL with water.

  NOTE: Prepare the buffer solution in a hood. Add the HCl to the solution slowly to minimize formation of dense, white fumes (the fumes are corrosive and can cause $NH_4^+$ and $Cl^-$ contamination in samples).

- Nitric Acid ($HNO_3$, 12 M, Baker Ultrex grade or equivalent).

- Phenol Red Indicator Solution (4 percent w/v).

- Sodium Acetate (NaOAc, 1.0 M)--Dissolve 8.20 g sodium acetate (Alfa ultrapure grade or equivalent) in water, then dilute to 100 mL.

- Sulfuric Acid ($H_2SO_4$, 18 M, Baker Ultrex grade or equivalent).

- Water--Water used in all preparations must conform to ASTM specifications for Type I water (ASTM, 1984). It is obtained from the Millipore Milli-Q water system.

- Aliquot Bottles--Clean aliquot bottles are required for the split samples and the seven aliquots prepared from each sample (see Tables 2.3 and 2.4 for the size and quantity required). The bottles are cleaned (using the procedure in Appendix A) and are supplied by an outside contractor.

- Indicating pH Paper (Range 8 to 9 and 1 to 3)

- Membrane Filters (0.45-µm pore size)

### 2.7.5 Procedure

Preparation of the seven aliquots and split samples is described in this section. All filtrations and aliquot 2 preparation are performed in the laminar-flow clean work station.

### 2.7.5.1 Preparation of Aliquots 1 and 4

Step 1--Complete aliquot labels for aliquots 1 and 4 and attach to containers. Assemble the filtration apparatus with a waste container as a collection vessel. Thoroughly rinse the filter holder and membrane filter in succession with 20 to 40 mL water, 20 mL 5 percent $HNO_3$ (Baker Instra-Analyzed grade), and 40 to 50 mL water.

Step 2--Rinse the filter holder and membrane with 10 to 15 mL of the sample to be filtered.

Step 3--Replace the waste container with the aliquot 1 container. Reapply vacuum (vacuum pressure must not exceed 12 in. Hg), and filter 10 to 15 mL of sample. Remove the vacuum. Rinse the aliquot 1 container with the 15 mL of filtered sample by slowly rotating the bottle so that the sample touches all surfaces. Discard the rinse sample and replace the container under the filter holder.

Step 4--Filter sample into the container until full.

Step 5--Transfer filtered sample into the aliquot 4 container (previously labeled) after first rinsing the container with 10 to 15 mL filtered sample.

Step 6--Return the aliquot 1 container to the filtration apparatus and collect additional filtered sample until the container is full.

If it is necessary to replace a membrane (due to clogging) before adequate filtered sample has been obtained, rinse the new membrane with 15 to 20 mL water, 10 to 15 mL 5 percent $HNO_3$, 40 to 50 mL water, and 10 to 15 mL sample prior to collecting additional sample.

Step 7--Between samples, remove the membrane and thoroughly rinse the filter holder with water.

Step 8--Preserve by adding concentrated $HNO_3$ to aliquot 1 and concentrated $H_2SO_4$ to aliquot 4 in 0.100-mL increments until the pH <2 (U.S. EPA, 1983). Check the pH by placing a drop of sample on indicating pH paper using a clean plastic pipet tip. Record on the aliquot label the volume of acid added.

Step 9--Store aliquots 1 and 4 at 4°C until ready to ship.

2.7.5.2 Preparation of Aliquot 2 - Total Extractable Aluminum (Barnes, 1975)

Step 1--Obtain a filtered portion of sample from the analyst performing filtrations.

Step 2--Rinse a clean, plastic 50-mL graduated centrifuge tube with three 10-mL portions of the filtered sample, then fill to the 25.0-mL mark.

Step 3--Add two to three drops phenol red indicator, 5.0 mL HOx reagent, and 2.0 mL $NH_4^+/NH_3$ buffer. Shake for 5 seconds. This should adjust the pH to 8.3 and the solution should turn red. If it does not turn red, rapidly adjust the pH by dropwise addition of 1 M $NH_4OH$ until the solution color changes to red. Add 10.0 mL MIBK, cap, and shake vigorously for 10 seconds using a rapid, end-to-end motion. (Note: Successful extraction depends on good agitation.) This entire process should take about 15 to 20 seconds. Open tube carefully after shaking, because pressure builds up.

Step 4--Centrifuge the sample to hasten separation of the aqueous and organic layers, then transfer the MIBK layer with a 5-mL micropipet to a 10-mL centrifuge tube. Securely cap tube.

Step 5--Complete a label for aliquot 2 and attach label to the container.

Step 6--Store the 10-mL tube containing aliquot 2 at 4°C in the dark until ready to ship.

Step 7--Discard the 50-mL centrifuge tube after a single use.

2.7.5.3 Preparation of Aliquot 3--Filtered sample for aliquot 3 is obtained similarly to that for aliquots 1 and 4, except that the filter holder used to filter aliquot 3 is never allowed to come into contact with nitric acid. This is CRUCIAL in preventing nitrate contamination. Previous experience indicates that even the most scrupulous water rinses did not remove all traces of a nitric acid rinse. Blanks still contained measurable nitrate.

Step 1--Soak filter holders for 24 hours in deionized water prior to first use.

Step 2--Complete an aliquot 3 label and attach label to the aliquot bottle. Assemble the filtration apparatus with a waste container as a collection vessel. Thoroughly rinse the filter holder and membrane filter with three 25-mL portions water, followed by 10 to 15 mL sample to be filtered.

Step 3--Replace the waste container with the aliquot 3 container and filter an additional 15 mL sample. Remove the container and rinse by slowly rotating the bottle so that the sample touches all surfaces. Discard the rinse sample and replace the container under the filter holder.

Step 4--Filter sample into the container until full.

If it is necessary to replace a membrane (due to clogging), rinse the membrane with three 20-mL portions water followed by 15 mL sample before collecting additional sample.

Step 5--Between samples, remove the membrane and thoroughly rinse the filter holder with water.

Step 6--Store at 4°C until ready to ship.

2.7.5.4 Preparation of Aliquots 5, 6, and 7--Aliquots 5, 6, and 7 are unfiltered aliquots.

Step 1--Complete aliquot 5, 6, and 7 labels and attach to the appropriate aliquot bottles. Transfer 15 to 20 mL sample to aliquot bottle and rinse by slowly rotating bottle so that sample touches all surfaces. Discard rinse.

Step 2--Fill aliquot bottle with unfiltered sample. Fill aliquot 5 bottle so that no headspace exists.

Step 3--Preserve by adding concentrated $HNO_3$ to aliquot 7 and concentrated $H_2SO_4$ to aliquot 6 in 0.100-mL increments until pH <2 (U.S. EPA, 1983). Check the pH by placing a drop of sample on indicating pH paper using a clean plastic pipet tip. Record the volume of acid added on the aliquot label.

Step 4--Store at 4°C until ready to ship.

2.7.5.5 Preparation of Split Samples--Three different split samples are prepared, depending upon their destination (Canada, EPA-Corvallis, or Norway). Descriptions of each split are listed in Table 2.4.

- EPA Corvallis splits--Prepare a split sample for Corvallis from all samples following the procedure for aliquot 1 preparation, with the exception that only 125 mL of sample need be filtered and collected. When sample volume limitations exist, other sample splits take precedence. Record the split code "E" on Form 2.

- Norwegian splits--Prepare a split sample for Norway from 90 samples in the Northeast (as directed by the QA manager) following the procedure for aliquot 5 preparation. Record the split code "N" on Form 2.

- Canadian splits--Prepare four split samples for Canada from 115 samples in the Northeast (as directed by the QA manager) following the procedure below:

  a. Splits C1, C3, and C4--Prepare following aliquot 5 procedure, except reduce volume and container size (not acid-washed) to 250 mL. (C4 requires only 125 mL sample.)

b. Split C2--Prepare following aliquot 7 procedure, except increase volume and container size (acid-washed) to 250 mL.

c. Split C4--Prepare following aliquot 5 procedure.

d. Record the split code "C" on Form 2.

## 2.8 References

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U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

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# 3.0 ANALYTICAL LABORATORY OPERATIONS

## 3.1 Summary of Operations

Samples are shipped from the field stations to the contract analytical laboratories for analysis. Each sample consists of seven aliquots, each processed in a different manner depending on the analytes for which the aliquot will be analyzed. A brief description of each aliquot and its corresponding analytes is given in Table 3.1.

After receipt, the analytes in each sample are quantified. The analyses must occur within the prescribed holding times (listed in Table 3.2) or a penalty is assessed against the lab. Strict QC requirements must be followed throughout the analyses. Finally, the sample results must be reported in the proper format, on a timely basis, for entry in the NSWS data base.

## 3.2 Sample Receipt and Handling

Samples are shipped to the contract laboratory by overnight delivery service. Upon receipt, measure the temperature inside the shipping container and record the temperature on the shipping form. Log in samples and ensure that the samples listed on the shipping form have actually been received. Note anything unusual (such as leaking samples) on the shipping form.

Store sample aliquots 2, 3, 4, 5 and 6 in the dark at 4°C when not in use. The samples must be stored at 4°C for 6 months or until notified by the QA manager.

Clean all labware that comes into contact with the sample (such as autosampler vials, beakers, etc.) as described in Appendix A.

## 3.3 Sample Analysis

The analytes to be determined in each sample and corresponding measurement techniques are listed in Table 3.3, and the method protocols are provided in sections 4 through 13. Each analyte must be determined within the holding times listed in Table 3.2.

TABLE 3.1. LIST OF ALIQUOTS, CONTAINERS, PRESERVATIVES, AND CORRESPONDING PARAMETERS TO BE MEASURED

| Aliquot[a] | Container | Preservative and Description | Parameters |
|---|---|---|---|
| 1 | 250 mL | Filtered, pH <2 with $HNO_3$ | Ca, Mg, K, Na, Mn, Fe |
| 2 | 10 mL | MIBK-HQ extract | Total extractable Al |
| 3 | 250 mL | Filtered | $Cl^-$, $F^-$, $SO_4^{2-}$, $NO_3^-$, $S_iO_2$ |
| 4 | 125 mL | Filtered, pH <2 with $H_2SO_4$ | DOC, $NH_4^+$ |
| 5 | 500 mL | Unfiltered | pH, acidity, alkalinity, specific conductance, DIC |
| 6 | 125 mL | Unfiltered, pH <2 with $H_2SO_4$ | Total P |
| 7 | 125 mL | Unfiltered, pH <2 with $HNO_3$ | Total Al |

[a] Aliquots 2, 3, 4, 5, and 6 must be stored at 4°C in the dark.

TABLE 3.2. LIST OF HOLDING TIMES

| Holding Time | Parameter |
|---|---|
| 7 days | $NO_3^-$,[a] pH,[b] Total extractable Al |
| 14 days | Alkalinity, acidity, specific conductance, DIC, DOC |
| 28 days | Total P, $NH_4^+$, $Cl^-$, $SO_4^{2-}$, $F^-$, $SiO_2$ |
| 6 months[c] | Ca, Mg, K, Na, total Al, Mn, Fe |

[a] Although the EPA (U.S. EPA, 1983) recommends that nitrate in unpreserved samples (un-acidified) be determined within 48 hours of collection, evidence exists (Peden, 1981 and APHA et al., 1985) that nitrate is stable for 2 to 4 weeks if stored in the dark at 4°C.

[b] Although the EPA (U.S. EPA, 1983) recommends that pH be measured immediately after sample collection, evidence exists (McQuaker et al., 1983) that it is stable for up to 15 days if stored at 4°C and sealed from the atmosphere. Seven days is specified here as an added precaution. The pH is also measured in a sealed sample at the field station within 12 hours of sample collection.

[c] Although the EPA (U.S. EPA, 1983) recommends a 6-month holding time for these metals, this study requires that all of the metals be determined within 28 days. This is to ensure that significant changes do not occur and to obtain data in a timely manner.

TABLE 3.3. LIST OF PARAMETERS AND CORRESPONDING MEASUREMENT METHODS

| Parameter | Method |
|---|---|
| 1. Acidity | Titration with Gran analysis |
| 2. Alkalinity | Titration with Gran analysis |
| 3. Aluminum, total | 202.2 AAS (furnace) |
| 4. Aluminum, total extractable | Extraction with 8-hydroxyquinoline into MIBK followed by AAS (furnace) |
| 5. Ammonium, dissolved | Automated colorimetry (phenate) |
| 6. Calcium, dissolved | AAS (flame) or ICPES |
| 7. Chloride, dissolved | Ion chromatography |
| 8. Fluoride, total dissolved | Ion-selective electrode and meter |
| 9. Inorganic carbon, dissolved | Instrument (acidification, $CO_2$ generation, IR detection) |
| 10. Iron, dissolved | AAS (flame) or ICPES |
| 11. Magnesium, dissolved | AAS (flame) or ICPES |
| 12. Manganese, dissolved | AAS (flame) or ICPES |
| 13. Nitrate, dissolved | Ion chromatography |
| 14. Organic carbon, dissolved | Instrument (uv-promoted oxidation, $CO_2$ generation, IR detection) |
| 15. pH | pH electrode and meter |
| 16. Phosphorus, total | Automated colorimetry (phosphomolybdate) |
| 17. Potassium, dissolved | AAS (flame) |
| 18. Silica, dissolved | Automated colorimetry (molybdate blue) |
| 19. Sodium, dissolved | AAS (flame) |
| 20. Sulfate, dissolved | Ion chromatography |
| 21. Specific conductance | Conductivity cell and meter |

## 3.4 Internal Quality Control Requirements

QC is an integral part of sample analysis. Method QC requirements common to all methods are detailed in this section. QC requirements specific to a single method are detailed in the description for that method.

### 3.4.1 Method Quality Control

Each method contains specific QC steps which must be performed to ensure data quality. Table 3.4 is a brief summary of the required QC checks as well as control limits and corrective actions for QC checks outside control limits. QC steps common to all (or most) of the methods are detailed in sections 3.4.1.1 through 3.4.1.4, while QC steps specific to a single method are detailed in the method protocol.

3.4.1.1 Calibration Verification QC Check Sample--After performing the calibration step for a method, verify the calibration (to ensure proper standard preparation, etc.) prior to sample analysis by analyzing a calibration QC check sample (QCCS). The QCCS is a known sample containing the analyte of interest at a concentration in the low- to mid-calibration range. Furthermore, the QCCS must be independent of the calibration standards.

For each batch of samples, analyze the calibration QCCS immediately after calibration, after every 10 sample analyses, and after the final sample analysis. Plot the measured analyte concentration in the QCCS on a control chart and develop the 95 percent and 99 percent confidence intervals. The 99 percent confidence interval must be within the limits given in Table 3.5. (The limits in Table 3.5 may be used as initial limits until enough data are obtained to generate a control chart.) If the 99 percent confidence interval is not within those limits, a problem exists with the experimental technique or the QCCS itself.

The measured analyte concentration in the QCCS must be within the 99 percent confidence interval. An acceptable result must be obtained prior to continuing sample determinations. If unacceptable results are obtained, repeat the calibration step and reanalyze all samples analyzed since the last acceptably analyzed QCCS.

## TABLE 3.4. SUMMARY OF INTERNAL METHOD QUALITY CONTROL CHECKS

| Parameter or Method | QC Check | Control Limits | Corrective Action[a] |
|---|---|---|---|
| Acidity, Alkalinity, pH | 1. Titrant standardization cross-check. | 1. Relative difference <5%. | 1. Restandardize titrants. |
| | 2. Electrode calibration (Nernstian response check). | 2. Slope = 1.00 ± 0.05. | 2. Recalibrate or replace electrode. |
| | 3. pH QCCS (pH 4 and 10) analysis. | 3. pH 4 = 4.00 ± 0.05.<br>pH 10 = 10.00 ± 0.05. | 3. Recalibrate electrode. |
| | 4. Blank analysis (salt spike). | 4. \|Blank\| $\leq$10 µeq/L. | 4. Prepare fresh KCl spike solution. |
| | 5. Duplicate analysis. | 5. RSD $\leq$10%. | 5. Refine analytical technique. Analyze another duplicate. |
| | 6. Protolyte comparison. | 6. See method (Section 4). | 6. See method (Section 4). |
| Ions ($Cl^-$, $F^-$, $NH_4^+$, $NO_3^-$, $SO_4^{2-}$), Metals (Al, Ca, Fe, K, Mg, Mn, Na), $SiO_2$, Total P, DIC, DOC Specific Conductance | 1a. Initial QCCS analysis (calibration and verification). | 1a,b. The lesser of the 99% CI or value given in Table 3.5. | 1a. Prepare new standards and recalibrate. |
| | b. Continuing QCCS analysis (every 10 samples). | | b. Recalibrate. Reanalyze associated samples. |
| | 2a. Detection limit determination (weekly). | 2a. DL < values in Table 1.1. | 2a,b. Optimize instrumentation and technique. |
| | b. DL QCCS analysis (daily, metals and total P only). | b. %Recovery = 100 ±20%. | |
| | 3. Blank analysis. | 3a. Blank $\leq$2 x DL (except sp. cond.). | 3a,b. Determine and eliminate contamination source. Prepare fresh blank solution. Reanalyze associated samples. |
| | | b. Blank $\leq$0.9 µS/cm (sp. cond. only). | |
| | 4. Duplicate analysis. | 4. Duplicate precision (RSD) $\leq$ values given in Table 1.1. | 4. Investigate and eliminate source of imprecision. Analyze another duplicate. |
| | 5. Matrix spike (except total ext. Al, DIC, and sp. cond.). | 5. %Recovery = 100 ± 15%. | 5. Analyze 2 additional spikes. If one or both outside control limits, analyze sample batch by method of standard additions. |
| | 6. Resolution test (IC only). | 6. Resolution $\geq$60%. | 6. Clean or replace separator column. Recalibrate. |

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[a] Assuming QC check is outside control limits.

TABLE 3.5. MAXIMUM CONTROL LIMITS FOR QUALITY CONTROL SAMPLES

| Parameter | Maximum Control Limit for QC Sample (% Deviation from Theoretical Concentration of QC Sample) |
|---|---|
| Al, total extractable | ±20% |
| Al, total | ±20% |
| Ca | ±5% |
| $Cl^-$ | ±5% |
| DIC | ±10% |
| DOC | ±10% |
| $F^-$, total | ±5% |
| Fe | ±10% |
| K | ±5% |
| Mg | ±5% |
| Mn | ±10% |
| Na | ±5% |
| $NH_4^+$ | ±10% |
| $NO_3^-$ | ±10% |
| P, total | ±20% |
| $SiO_2$ | ±5% |
| $SO_4^{2-}$ | ±5% |
| Specific conductance | ±2% |

3.4.1.2 Detection Limit Determination and Verification--Determine the detection limit weekly for all parameters (except pH alkalinity, acidity, and specific conductance for which the term detection limit does not apply). For the NSWS, the detection limit is defined as three times the standard deviation of 10 nonconsecutive reagent or calibration blank analyses. In the case where a signal is not obtained for a blank analysis (such as in ion chromatographic analyses or autoanalyzer analyses), a lowconcentration standard (concentration about three to four times the detection limit) is analyzed rather than a blank. Detection limits must not exceed the values listed in Table 1.1. If a detection limit is not met, refine the analytical technique and optimize any instrumentation variables until the detection limit is achieved.

To verify the detection limit for the determination of metals and total P daily, analyze a detection limit QCCS after calibration and prior to sample analysis. The detection limit QCCS must contain the analyte of interest at two to three times the detection limit. The measured concentration must be within 20 percent of the true concentration. If it is not, the detection limit is questionable. Determine the detection limit as described above.

3.4.1.3 Blank Analysis--Once per batch analyze a calibration blank as a sample. The calibration blank is defined as a "0" mg/L standard (contains only the matrix of the calibration standards). The measured concentration of the calibration blank must be less than twice the instrumental detection limit. If not, the blank is contaminated or the calibration is in error at the low end. Prior to sample analysis, investigate and eliminate any contamination source and repeat the calibration.

Prepare and analyze a reagent blank for the three methods which require sample preparation (dissolved $SiO_2$, total P, and total Al). A reagent blank contains all the reagents (in the same quantities) used in preparing a real sample for analysis. Process in the same manner (digestions, etc.) as a real sample. The measured concentration of the reagent blank must be less than twice the required detection limit (Table 1.1). If it is not, the reagent blank is contaminated. Investigate and eliminate the contamination source. Prepare and analyze a new reagent blank and apply the same criteria. Reanalyze all samples associated with the contaminated blank when the contamination is eliminated. Contact the QA manager if a contaminated reagent blank problem cannot be rectified.

Prepare one reagent blank with each set of samples processed at one time. For example, if two sample batches are processed together, only one reagent blank is necessary. Report the concentration of the single reagent blank for both batches. On the other hand, if a sample batch is split into groups that are processed at different times, a reagent blank is necessary for each group. In this case, report all reagent blank values for the batch. (Identify in a cover letter which reagent blank values are associated with which samples.)

3.4.1.4 Duplicate Sample Analysis--Prepare and analyze one sample per batch in duplicate. If possible, for duplicate analysis choose a sample containing analyte at a concentration greater than five times the detection limit. Calculate the relative standard deviation (RSD) between duplicates. The duplicate precision (RSD) must not exceed the value given in Table 1.1. If duplicate RSD values fall outside the values given in Table 1.1, a problem exists (such as instrument malfunction, calibration drift, etc.). After finding and resolving the problem, analyze a second sample in duplicate. Acceptable duplicate sample results must be obtained prior to continuing sample analysis.

$$\% \text{ RSD} = \frac{S}{\bar{x}} \times 100$$

$$S = \left( \frac{\Sigma(\bar{x} - x)^2}{n-1} \right)^{1/2}$$

3.4.1.5 Matrix Spike Analysis--Prepare one matrix spike with each batch by spiking a portion of a sample with a known quantity of analyte. The spike concentration must be the larger of two times the endogenous level or ten times the required detection limit. Also, the volume of the spike added must be negligible (less than or equal to 0.001 of the sample aliquot volume). Calculate the percent recovery of the spike as follows:

$$\% \text{ spike recovery} = \frac{\left( \begin{array}{c}\text{measured}\\ \text{concentration}\\ \text{of sample}\\ \text{plus spike}\end{array} - \begin{array}{c}\text{measured}\\ \text{concentration}\\ \text{of unspiked}\\ \text{sample}\end{array} \right)}{(\text{actual concentration of spike added})} \times 100$$

The spike recovery must be 100 ± 15 percent. If the recovery is not acceptable, spike and analyze two additional, different samples. If either recovery is unacceptable, analyze the entire batch by the method of standard additions. The method of standard addition involves analyzing the sample, sample plus a spike at about the endogenous level, and sample plus a spike at about twice the endogenous level.

NOTE: Matrix spikes for graphite furnace atomic absorption spectroscopy (GFAA) analyses may not be added directly in the furnace.

The concentration of the matrix spike must not exceed the instrument linear dynamic range. For this reason, the matrix spike concentration for furnace analyses must be chosen judiciously and may be different than suggested above.

Similarly, care must be taken to avoid exceeding the linear range when performing standard additions for GFAA analyses. The samples may be diluted and the spike levels may be adjusted so that the linear range is not exceeded.

### 3.4.2 Overall Internal Quality Control

Once each parameter in a sample has been determined, two procedures exist for checking the correctness of analyses. These procedures are outlined in sections 3.4.2.1 and 3.4.2.2.

3.4.2.1 Anion-Cation Balance--Theoretically, the acid neutralizing capacity (ANC) of a sample equals the difference between the concentration (eq/L) of cations and the anions in a sample (Kramer, 1982). In practice, this is rarely true due to analytical variability and to ions that are present but not measured. For each sample, calculate the percent ion difference (%ID) as follows:

$$\%\text{ Ion Difference} = \frac{\text{ANC} + \Sigma\text{ anions} - \Sigma\text{ cations}}{\text{TI}} \times 100$$

$$\text{TI (Total ion strength)} = \Sigma\text{ anions} + \Sigma\text{ cations} + \text{ANC} + 2\,[\text{H}^+]$$

$$\Sigma\text{ anions} = [\text{Cl}^-] + [\text{F}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}]$$

$$\Sigma\text{ cations} = [\text{Na}^+] + [\text{K}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{NH}_4^+]$$

$$\text{ANC} \cong [\text{ALK}]$$

$$[\text{H}^+] = (10^{-\text{pH}}) \times 10^6\ \mu\text{eq/L}$$

All concentrations are expressed as microequivalents/liter (µeq/L). Table 3.6 lists factors for converting mg/L to µeq/L for each of the parameters.

The %ID must not exceed the limits given in Table 3.7. An unacceptable value for %ID indicates the presence of unmeasured ions or an analytical error in the sample analysis. For the surface waters sampled, the ions included in the %ID calculation are expected to account for 90 to 100 percent of the ions in a sample. Note that the ANC term in the calculation accounts for protolyte ions that are not specifically determined (such as organic acids and bases).

Examine the data from samples that do not meet the %ID criteria for possible causes of unacceptable %ID. Often, the cause is improper data reporting (misplaced decimal point, incorrect data reduction, switched sample ID's, etc.). After examining the data, redetermine any parameter that is suspect. If an explanation for the poor %ID cannot be found and the problem cannot be corrected, contact the QA manager at EMSL-Las Vegas for further guidance.

TABLE 3.6 FACTORS TO CONVERT mg/L TO µeq/L

| Ion | Factor (µeq/L per mg/L) |
|---|---|
| $Ca^{2+}$ | 49.9 |
| $Cl^-$ | 28.2 |
| $F^-$ | 52.6 |
| $K^+$ | 25.6 |
| $Mg^{2+}$ | 82.3 |
| $Na^+$ | 43.5 |
| $NH_4^+$ | 55.4 |
| $NO_3^-$ | 16.1 |
| $SO_4^{2-}$ | 20.8 |

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TABLE 3.7. CHEMICAL REANALYSIS CRITERIA

A. Anion-Cation Balance

| Total Ion Strength (μeq/L) | Maximum % Ion Difference[a] |
|---|---|
| <50 | 60 |
| ≥50<100 | 30 |
| ≥100 | 15 |

B. Specific Conductance

| Measured Conductance (μS/cm) | Maximum % Conductance Difference[a] |
|---|---|
| <5 | 50 |
| ≥5<30 | 30 |
| ≥30 | 20 |

---

[a] If the absolute value of the percent difference exceeds these values, the sample is reanalyzed. When reanalysis is indicated, the data for each parameter are examined for possible analytical error. Any suspect results are then redetermined and the above percent differences are recalculated (Peden, 1981). If the differences are still unacceptable or no suspect data are identified, the QA manager should be contacted for guidance.

3.4.2.2 Conductivity Balance--Estimate the specific conductance of a sample by summing the equivalent conductances for each measured ion. Calculate the equivalent conductance for each ion by multiplying the ion concentration by the appropriate factor in Table 3.8 (only major ions are included in the calculation). Calculate the percent conductance difference (%CD) as follows:

$$\text{\% Conductance Difference} = \frac{\text{calculated cond. - measured cond.}}{\text{measured conductance}} \times 100$$

The %CD must not exceed the limits listed in Table 3.7. As with the %ID calculation, an unacceptable value for %CD indicates either the presence of unmeasured ions or an analytical error in the sample analysis. For the surface waters sampled, the ions included in the %CD calculation are expected to account for 90 to 100 percent of the ions in a sample. However, in contrast to the %ID calculation, there is no term in the %CD calculation to account for protolytes not specifically determined.

Examine the data from samples that do not meet the %CD criteria for possible causes of the unacceptable %CD, such as improper data reporting or analysis. The presence or absence of unmeasured protolytes can be tested by the procedures described in section 4. Note that the absence of unmeasured protolytes is positive evidence that the %CD exceeds the maximum difference due to analytical error. Redetermine any parameter that is identified as suspect. If an explanation for the poor %CD cannot be found and the problem cannot be corrected, contact the QA manager at EMSL-Las Vegas for further guidance.

## 3.5 Data Reporting

Record the results from each method on the data form indicated in Table 3.9 (blank data forms are included in Appendix B). Report results to the number of decimal places in the actual detection limit. However, report no more than four significant figures. Sample results from reanalyzed samples (occasionally samples are reanalyzed for QC reasons) are annotated by the letter R. Results obtained by standard additions are annotated by the letter G. These and other data qualifiers are listed in Table 3.10. After the forms are completed, the laboratory manager must sign them, indicating he has reviewed the data and that the samples were analyzed exactly as described in this manual. All deviations from the manual require the authorization of the QA manager prior to sample analysis.

TABLE 3.8. CONDUCTANCE FACTORS OF IONS[a]

| Ion | Specific Conductance (μS/cm at 25°C) per mg/L | Ion | Specific Conductance (μS/cm at 25°C) per mg/L |
|---|---|---|---|
| $Ca^{2+}$ | 2.60 | $Na^+$ | 2.13 |
| $Cl^-$ | 2.14 | $NH_4^+$ | 4.13 |
| $CO_3^{2-}$ | 2.82 | $SO_4^{2-}$ | 1.54 |
| $H^+$ | $3.5 \times 10^5$ (per mole/L) | $NO_3^-$ | 1.15 |
| $HCO_3^-$ | 0.715 | $K^+$ | 1.84 |
| $Mg^{2+}$ | 3.82 | $OH^-$ | $1.92 \times 10^5$ (per mole/L) |

$$[H^+] \text{ moles/L} = 10^{-pH}$$

pH = pH determined at V=0 of the acidity titration.

$$[OH^-] = \frac{Kw}{[H^+]}$$

$$HCO_3^- = \frac{5.080\ [DIC(mg/L)]\ [H^+]\ K_1}{[H^+]^2 + [H^+]\ K_1 + K_1\ K_2}$$

$$CO_3^{2-} = \frac{4.996\ [DIC(mg/L)]\ K_1 K_2}{[H^+]^2 + [H^+] K_1 + K_1\ K_2}$$

$$K_1 = 4.4463 \times 10^{-7} \quad K_2 = 4.6881 \times 10^{-11}$$

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[a] APHA et al., 1985 and Weast, 1972.

TABLE 3.9. LIST OF DATA FORMS

| Data Form | Description |
|---|---|
| 11 | Summary of sample results |
| 12[a] | QCCS pH results |
| 13 | Alkalinity and acidity results |
| 14[a] | QC data for alkalinity and acidity analysis |
| 15[a] | Specific conductance (measured and calculated) |
| 16[a] | Anion-cation balance calculations |
| 17 | Ion chromatography resolution test form |
| 18 | QA (detection limits) |
| 19 | Sample holding times summary |
| 20 | Blank and QCCS results |
| 21 | Matrix spike results |
| 22 | Duplicate results |
| 23 | Standard addition results |

[a] Form is not required but is recommended for internal lab use.

Copies of raw data must be submitted as requested by the program manager. All original raw data must be retained by the lab until notified otherwise. Raw data include data system printouts, chromatograms, notebooks, QC charts, standard preparation data, and all information pertinent to sample analysis.

TABLE 3.10. NATIONAL SURFACE WATER SURVEY DATA QUALIFIERS

| Qualifier | Indicates |
|---|---|
| F | Result outside QA criteria (with consent of QA manager) |
| G | Result obtained from method of standard additions |
| H | Holding time exceeded criteria (Form 19 only) |
| J | Result not available; insufficient sample volume shipped |
| K | Result not available; entire aliquot not shipped |
| L | Result not available; analytical interference |
| M | Result not available; sample lost or destroyed by lab |
| N | Not required |
| P | Result outside QA criteria, but insufficient volume for reanalysis |
| Q | Result outside QA criteria |
| R | Result from reanalysis |
| S | Contamination suspected |
| T | Leaking container |
| U | Result not required by procedure |
| V | Anion-cation balance outside criteria due to DOC |
| W | % Difference (%D) calculation (Form 14) outside criteria due to high DOC |
| Y | Available for miscellaneous comments |
| Z | Available for miscellaneous comments |

## 3.6 References

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1985. Standard Methods for the Examination of Water and Wastewater, 16th Ed. APHA, Washington, D.C.

Kramer, J. R., 1982. Alkalinity and Acidity. In: R. A. Minear, L. H. Keith (eds.), Water Analysis. Vol. 1. Inorganic Species, Part 1. Academic Press, Orlando, Florida.

McQuaker, N. R., P. D. Kluckner, and D. K. Sandberg, 1983. Chemical Analysis of Acid Precipitation: pH and Acidity Determinations. Environ. Sci. Technol., v. 17 n. 7, pp. 431-435.

Peden, M. E., 1981. Sampling, Analytical, and Quality Assurance Protocols for the National Atmospheric Deposition Program. Paper presented at October 1981 ASTM D-22 Symposium and Workshop on Sampling and Analysis of Rain. ASTM, Philadelphia, Pennsylvania.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

Weast, R. C. (ed.), 1972. CRC Handbook of Chemistry and Physics, 53rd Ed. CRC Press, Cleveland, Ohio.

# 4.0 DETERMINATION OF ACIDITY, ALKALINITY, AND pH

## 4.1 Scope and Application

This procedure is applicable to the determination of pH, alkalinity, and acidity in weakly buffered natural waters of low ionic strength. The terms alkalinity and acidity refer to the acid neutralizing capacity (ANC) and base neutralizing capacity (BNC) of systems which are based on the carbonate ion system. (The soluble reacting species are $H_2CO_3$, $HCO_3^-$, and $CO_3^{2-}$.) For calculation purposes, it is assumed that the lakes in this survey are represented by a carbonate ion system; hence, the alkalinity and acidity definitions are made in relation to the carbonate ion species (Kramer, 1982; Butler, 1982).

## 4.2 Summary of Method

Samples are titrated with standardized acid and base while monitoring and recording the pH. The acidity (Acy) and alkalinity (Alk) are determined by analyzing the titration data using a modified Gran analysis technique (Kramer, 1982; Butler, 1982; Kramer, 1984; Gran, 1952).

The Gran analysis technique defines the Gran functions $F_1$ and $F_2$ based upon sample volume, acid (base) volume added, and carbonate dissociation constants. The Gran functions are calculated for several data pairs (volume of titrant added, resulting pH) from a titration. The data pairs are chosen so that they cross the alkalinity and acidity equivalence points. When the Gran functions are plotted *versus* volume of titrant added, the linear portion of each curve can be interpolated to the equivalence point.

The pH is determined prior to the start of the titrations with the electrode used during the titration. (U.S. EPA, 1983; McQuaker et al., 1983; NBS, 1982).

The air-equilibrated pH is determined similarly after equilibrating the sample with 300 ppm $CO_2$ in air. Air equilibration is expected to normalize pH values by factoring out the day-to-day and seasonal fluctuations in dissolved $CO_2$ concentrations.

## 4.3 Interferences

No interferences are known.

## 4.4 Safety

The standards, sample types, and most reagents pose no hazard to the analyst. Protective clothing (lab coat and gloves) and safety glasses must be used when handling concentrated acids and bases.

Gas cylinders must be secured in an upright position.

## 4.5 Apparatus and Equipment

- pH/mV Meter--A digital pH/mV meter capable of measuring pH to ±0.01 pH unit, potential to ±1 mV, and temperature to ±0.5°C must be used. It must also have automatic temperature compensation capability.
- pH Electrodes--High-quality, low-sodium glass pH and reference electrodes must be used. (Gel-type reference electrodes must not be used.) A combination electrode is recommended (such as the Orion Ross combination pH electrode or equivalent), and the procedure is written assuming one is used.
- Buret--A microburet capable of precisely and accurately delivering 10 to 50 µL must be used (relative error and standard deviation less than 1 percent).

  NOTE: A commercial titration instrument meeting the same specifications may be used in place of the pH/mV meter, pH electrodes, and buret.
- Teflon-coated Stir Bars
- Variable-Speed Magnetic Stirrer
- Plastic Gas Dispersion Tube

  NOTE: Glass dispersion tubes must not be used because they can add alkalinity to a sample. Plastic dispersion tubes are available in most fish-aquarium supply stores.

## 4.6 Reagents and Consumable Materials

- Carbon Dioxide Gas (300 ppm $CO_2$ in Air)--Certified Standard Grade
- Hydrochloric Acid Titrant (0.01N HCl)--Add 0.8 mL concentrated hydrochloric acid (HCl, 12N, ACS reagent grade or equivalent) to 500 mL water, then dilute to 1.00 L with water. Standardize as described in section 4.8.1.
- Nitrogen Gas ($N_2$)--$CO_2$-free
- Potassium Chloride Solution (0.10 M KCl)--Dissolve 7.5 g KCl (Alfa Ultrapure or equivalent) in water, then dilute to 1.00 L with water.

- Potassium Hydrogen Phthalate (KHP)--Dry 5 to 10 g KHP (ACS-certified primary standard grade or equivalent) at 110°C for 2 hours, then store in a desiccator.

- pH Calibration Buffers (pH 4, 7, and 10)--NBS-traceable pH buffers at pH values of 4, 7, and 10.

- pH QC Samples (pH 4 and 10)--pH 4 QC sample - dilute 1.00 mL standardized 0.01N HCl titrant to 100.00 mL with water. The theoretical pH is calculated by

$$pH = -\log\left(\frac{N_{HCl}}{100}\right)$$

- pH 10 QC sample - Dilute 1.00 mL of the standardized 0.01N NaOH titrant to 100.00 mL with water. The theoretical pH is calculated by

$$pH = 14 + \log\left(\frac{N_{NaOH}}{100}\right)$$

- Sodium Carbonate ($Na_2CO_3$)--Dry 5 to 10 g $Na_2CO_3$ (ACS certified primary standard grade or equivalent) at 110°C for 2 hours, then store in a desiccator.

- Sodium Hydroxide Stock Solution (50 percent w/v NaOH)--Dissolve 100 g NaOH (ACS reagent grade or equivalent) in 100 mL water. After cooling and allowing any precipitate to settle (may be hastened by centrifugation), transfer the supernatant to a polyethylene bottle. Store tightly capped and avoid atmospheric exposure.

- Sodium Hydroxide Titrant (0.01 N NaOH)--Dilute 0.6 to 0.7 mL 50 percent NaOH to 1.0 L with water. Standardize as described in section 4.8.2.

- Water--Water used to prepare reagents and standards must conform to ASTM specifications for Type I water (ASTM, 1984).

## 4.7 Sample Collection, Preservation, and Storage

The sample for which acidity, alkalinity, and pH is to be determined is delivered to the lab in a 500-mL amber polyethylene bottle (aliquot 5). Store at 4°C and minimize atmospheric exposure.

## 4.8 Calibration and Standardization

### 4.8.1 Standardization of HCl Titrant

Step 1--Weigh about 1 g anhydrous $Na_2CO_3$ to the nearest 0.1 mg, dissolve in water, then dilute to 1.000 L. Calculate the concentration by the following equation.

$$N_{Na_2CO_3} = \frac{\text{wt. } Na_2CO_3 \text{ g}}{\frac{106.00 \text{ g}}{\text{mole}} \times \frac{1 \text{ mole}}{2 \text{ eq}}} \times \frac{1}{1L}$$

NOTE: This solution is to be freshly prepared just before use.

Step 2--Calibrate the pH meter and electrode as recommended by the manufacturer.

Step 3--Pipet 1.00 mL standard $Na_2CO_3$ plus 40.00 mL $CO_2$-free water into a clean, dry titration vessel. Add a Teflon-coated stir bar and stir at a medium speed (no visible vortex).

Step 4--Immerse the pH electrode and record the pH when a stable reading is obtained.

Step 5--Add a known volume of the HCl titrant and record the pH when a stable reading is obtained. Use the following table as a guide to the volume of titrant that should be added in different pH ranges:

| pH | Maximum Volume Increment of HCl Titrant (mL) |
|---|---|
| >7.5 | 0.2 |
| 4-7.5 | 0.1 |
| <4 | 0.2 |

Continue the titration until the pH <4. Obtain at least seven data points in the range pH 4 to 7.

Step 6--Calculate $F_{1b}$ for each data pair (volume acid added, pH) with pH in the range 4 to 7:

$$F_{1b} = (V_s + V) \left[ \frac{V_s C}{(V_s + V)} \left( \frac{[H^+]K_1 + 2 K_1 K_2}{[H^+]^2 + [H^+]K_1 + K_1 K_2} \right) + \frac{K_w}{[H^+]} - [H^+] \right]$$

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$F_{1b}$ = Gran function
$V_s$ = Initial sample volume = 41.00 mL
$V$ = Volume of HCl added in mL
$C$ = N $Na_2CO_3$/(2 x dilution factor)
$[H^+]$ = $10^{-pH}$
$K_1$ = $4.4463 \times 10^{-7}$
$K_2$ = $4.6881 \times 10^{-11}$
$K_w$ = $1.0123 \times 10^{-14}$

Step 7--Plot $F_{1b}$ versus V. Using the points on the linear portion of the plot, perform a linear regression of $F_{1b}$ on V to obtain the coefficients of the line

$$F_{1b} = a + bV$$

The correlation coefficient should exceed 0.999. If it does not, reexamine the plot to make sure only points on the linear portion are used in the linear regression.

Step 8--Calculate the equivalence volume, $V_1$, by

$$V_1 = -a/b$$

then calculate the HCl normality by

$$N_{HCl} = \frac{N\ Na_2CO_3 \times V\ Na_2CO_3}{V_1}$$

Step 9--Repeat the titration and calculation three times (steps 3 through 8). Calculate an average $N_{HCl}$ and standard deviation. The RSD must be less than 2 percent. If it is not, the entire standardization must be repeated until it is less than 2 percent.

Step 10--The concentration of every new batch of HCl titrant must be cross checked using the procedure described in Section 4.8.2.2.

Step 11--Store in a clean polyethylene bottle. Although the HCl titrant is stable, it must be restandardized monthly.

NOTE: An example of an HCl standardization is given in Appendix C.

### 4.8.2 Standardization of NaOH Titrant

Every batch of NaOH titrant is initially standardized against KHP (section 4.8.2.1) and the standardization cross-checked against standardized HCl titrant (section 4.8.2.2). Thereafter, it is restandardized daily against the HCl titrant (section 4.8.2.3).

### 4.8.2.1 Initial NaOH Standardization

Step 1--Weigh about 0.2 g KHP to the nearest 0.1 mg, dissolve in water, then dilute to 1.000 L. Calculate the normality of the solution by the following equation.

$$N_{KHP} = \frac{\text{wt. KHP g}}{\frac{204.22\text{ g}}{\text{eq}}} \times \frac{1}{1\text{ L}}$$

Step 2--Calibrate the pH electrode and meter as recommended by the manufacturer.

Purge the titration vessel with $CO_2$-free nitrogen, then pipet 5.00 mL standard KHP solution and 20.00 mL $CO_2$-free water into the vessel. Maintain a $CO_2$-free atmosphere above the sample throughout the titration. Add a Teflon stir bar and stir at a medium speed (no visible vortex).

Step 3--Immerse the pH electrode and record the reading when it stabilizes.

Step 4--Titrate with the 0.01N NaOH using the increments specified in the table below. Record the volume and pH (when stable) between additions. Continue the titration until the pH >10. Obtain at least four data points in the pH range 5 to 7 and four data points in the pH range 7 to 10.

| pH | Maximum Volume Increment of NaOH Titrant (mL) |
|---|---|
| <5 | 0.10 |
| 5 to 9 | 0.05 |
| >9 | 0.2 |

Step 5--Calculate $F_{3b}$ for each data pair (volume added, pH) with a pH 5-10.

$$F_{3b} = (V_s + V)\left[\frac{V_s C}{(V_s + V)}\left(\frac{[H^+]K_1 + 2[H^+]}{[H^+]^2 + [H^+]K_1 + K_1 K_2}\right) + [H^+] - \frac{K_w}{[H^+]}\right]$$

$F_{3b}$ = Gran function
$V_s$ = Initial sample volume = 25.00 mL
$V$ = Volume of NaOH added (mL)
$C$ = N KHP corrected for initial dilution = N KHP/5
$[H^+]$ = $10^{-pH}$
$K_1$ = $1.3 \times 10^{-3}$
$K_2$ = $3.9 \times 10^{-6}$
$K_w$ = $1.01 \times 10^{-14}$

Step 6--Plot $F_{3b}$ versus V. Using the points on the linear portion of the plot, perform a linear regression of $F_{3b}$ on V to obtain the coefficients of the line

$$F_{3b} = a + bV$$

The correlation coefficient should exceed 0.999. If it does not, examine the plot to ensure that only points on the linear portion are used in the linear regression.

Step 7--Calculate the equivalence volume, $V_3$, by

$$V_3 = -a/b$$

then calculate the NaOH normality by

$$N_{NaOH} = \frac{N_{KHP} \times V_{KHP}}{V_3}$$

Step 8--Perform the titration and calculation a total of three times. Calculate an average $N_{NaOH}$ and standard deviation. The RSD must be less than 2 percent. If not, the entire standardization must be repeated until the RSD is less than 2 percent.

### 4.8.2.2 NaOH-HCl Standardization Cross-Check

Step 1--Purge a titration vessel with $CO_2$-free nitrogen, then pipet 0.500 mL of 0.01N NaOH and 25.00 mL of $CO_2$-free water into the vessel. Maintain a $CO_2$-free atmosphere above the sample. Add a Teflon stir bar and stir at a medium speed.

Step 2--Immerse the pH electrode and record the reading when it stabilizes.

Step 3--Titrate with the standardized 0.01N HCl using the increments specified in the table below. Record the volume and pH (when stable) between additions. Continue the titration until the pH is less than 3.5. Obtain at least seven data points in the pH range 4 to 10.

| pH | Maximum Volume Increment of HCl Titrant (mL) |
|---|---|
| >10 | 0.2 |
| 10 to 4 | 0.05 |
| <4 | 0.2 |

Step 4--Calculate $F_1$ for each data pair (V, pH) with a pH 4 to 10.

$$F_1 = (V_s + V)\left(\frac{K_w}{[H^+]} - [H^+]\right)$$

$F_1$ = Gran function
$V_s$ = Initial sample volume = 25.5 mL
$V$ = Volume of HCl added (mL)
$K_w$ = $1.01 \times 10^{-14}$
$[H^+]$ = $10^{-pH}$

Step 5--Plot $F_1$ versus V. Using the points on the linear portion of the plot, perform a linear regression of $F_1$ on V to obtain the coefficients of the line

$$F_1 = a + bV$$

The correlation coefficient should exceed 0.999. If not, reexamine the plot to ensure that only points on the linear portion are used in the linear regression.

Step 6--Calculate the equivalence volume, $V_1$, by

$$V_1 = -a/b$$

then calculate the HCl normality (designated as $N'_{HCl}$) by

$$N'_{HCl} = \frac{N_{NaOH} \times V_{NaOH}}{V_1}$$

$V_{NaOH}$ = 0.500

Step 7--Calculate the absolute relative percent difference (RPD) between $N'_{HCl}$ and $N_{HCl}$ (normality determined in section 4.8.1) by

$$RPD = \left| \frac{N'_{HCl} - N_{HCl}}{0.5\,(N'_{HCl} + N_{HCl})} \right| \times 100$$

The absolute RPD must be less than 5 percent. If not, then a problem exists in the acid and/or the base standardization (bad reagents, out-of-calibration burets, etc.). The problem must be identified and both procedures 4.8.1 and 4.8.2 must be repeated until the RPD calculated above is less than 5 percent.

4.8.2.3 Daily NaOH Standardization

Step 1--Calibrate the pH meter and electrode as recommended by the manufacturer.

Step 2--Purge the titration vessel with $CO_2$-free nitrogen, then pipet 1.000 mL NaOH titrant plus 25.00 mL $CO_2$-free water into the vessel. Maintain a $CO_2$-free nitrogen atmosphere above the sample. (Smaller volumes of NaOH may be used. A known volume of $CO_2$-free water should be added to bring solution to a convenient volume.) Add a Teflon stir bar and stir at a medium speed.

Step 3--Immerse the pH electrode and record the reading when it stabilizes.

Step 4--Titrate with the standardized HCl titrant using the increments specified in the table below. Record the volume and pH (when stable) between additions. Continue the titration until the pH <4. Obtain at least seven data points in the pH range 4 to 10.

| pH | Maximum Volume Increment of HCl Titrant (mL) |
|---|---|
| >10 | 0.2 |
| 4 to 10 | 0.05 |
| <4 | 0.2 |

Step 5--Calculate $F_1$ for each data pair (volume acid added, pH) with a pH 4 to 10:

$$F_1 = (V_s + V)\left(\frac{K_w}{[H^+]} - [H^+]\right)$$

$F_1$ = Gran function
$V_s$ = Initial sample volume = 26.00 mL
$V$ = Volume of HCl added
$K_w$ = $1.01 \times 10^{-14}$
$[H^+]$ = $10^{-pH}$

Step 6--Plot $F_1$ versus V. Using the points on the linear portion of the plot, perform a linear regression of $F_1$ on V to obtain the coefficients of the line

$$F_1 = a + bV$$

The correlation coefficient should exceed 0.999. If it does not, reexamine the plot to make sure that only points on the linear portion are used in the linear regression.

Step 7--Calculate the equivalence volume, $V_1$, by

$$V_1 = -a/b$$

then calculate the NaOH normality by

$$N_{NaOH} = \frac{N_{HCl} \times V_1}{V_{NaOH}}$$

Step 8--Perform the titration and calculation twice more (steps 2 through 7). Calculate an average $N_{NaOH}$ and standard deviation. The RSD must be less than 2 percent. If it is not, the entire standardization must be repeated until the RSD is less than 2 percent.

Because the NaOH titrant can readily deteriorate through exposure to the air, every effort must be made to prevent its exposure to the air at all times. Furthermore, it must be standardized daily or before every major work shift. Store in a linear polyethylene or Teflon container with a $CO_2$-free atmosphere, e.g., under $CO_2$-free air, nitrogen, or argon.

NOTE: An example of NaOH standardization is given in Appendix C.

### 4.8.3 Calibration and Characterization of Electrodes

Separate electrodes must be used for the acid and base titration. Each new electrode pair must be rigorously evaluated for Nernstian response, using the procedure described in section 4.8.3.1, prior to analyzing samples. After the initial electrode evaluation, the electrodes are calibrated daily using the procedure in section 4.8.3.2.

4.8.3.1 Rigorous Calibration Procedure--This procedure calibrates (in terms of H ion concentration) and evaluates the Nernstian response of an electrode. Also, it familiarizes the analyst with the electrode's characteristic response time.

Step 1--Following the manufacturer's instructions, calibrate the electrode and meter used for acid titrations with pH 7 and 4 buffer solutions and the electrode used for base titrations with pH 7 and 10 buffer solutions.

Step 2--Prepare a blank solution by pipetting 50.00 mL $CO_2$-free water and 0.50 mL 0.10M KCl into a titration vessel. Add a Teflon stir bar and stir at a medium speed using a magnetic stirrer.

Step 3--Titrate the blank with standardized 0.01N HCl using the increments specified in the table below. Continue the titration until the pH is 3.3 to 3.5. Record the pH between each addition, noting the time required for stabilization. Obtain at least seven data points that have a pH less than 4.

| pH | Maximum Volume Increment of HCl Titrant (mL) |
|---|---|
| >4 | 0.050 |
| <4 | 0.3 |

Step 4--Prepare a fresh aliquot of water and 0.10M KCl as in step 2.

Step 5--Under a $CO_2$-free atmosphere, titrate the blank with standardized 0.01N NaOH using the increments specified in the table below.

| pH | Maximum Volume Increment of NaOH Titrant (mL) |
|---|---|
| <10 | 0.10 |
| >10 | 0.20 |

Continue the titration until the pH is 10.5 to 11. Record the pH between each addition. Obtain at least 10 data points between pH 9 and 10.5.

Step 6--For each titration, calculate the pH for each data point using pH = -log [H+]. [H+] is calculated by

acid titration

$$[H^+] = \frac{V_A C_A}{V_S + V_A} \text{ in eq/L}$$

base titration

$$[H^+] = \frac{K_w}{\left(\frac{V_B\ C_B}{V_s + V_B}\right)} \text{ in eq/L}$$

$V_A$ = acid volume (in mL)
$C_A$ = HCl concentration in eq/L
$V_s$ = sample volume = 50.5 mL
$K_w$ = $1.01 \times 10^{-14}$
$V_B$ = base volume (in mL)
$C_B$ = NaOH concentration in eq/L

Step 7--For each titration, plot the measured pH versus the calculated pH (designated as pH*). Perform a linear regression on each plot to obtain the coefficients of the line

$$pH = a + b(pH^*)$$

The plots must be linear with $b = 1.00 \pm 0.05$ and $r > 0.999$. Typically, some nonlinearity exists in the pH region 6 to 8. This is most likely due to small errors in titrant standardization, impure salt solutions, or atmospheric $CO_2$ contamination. The nonlinear points should not be used in the linear regression.

If the plots are not linear and do not meet the specifications above, the electrode should be considered suspect. The electrode characterization must then be repeated. If unacceptable results are still obtained, the electrode must be replaced.

Step 8--The plots for both titrations should be coincident. Combine the data from both titrations and perform a linear least squares analysis on the combined data to obtain new estimates for the coefficients of

$$pH = a + b(pH^*)$$

The electrodes are now calibrated. Do not move any controls on the meter.

If the two plots are not coincident (i.e., the coefficients a and b do not overlap), the characterization must be repeated. If the plots are still not coincident, the electrode must be replaced.

4.8.3.2 Daily Calibration Procedure--Generally, the calibration curve prepared above is stable from day to day. This daily calibration is designed to verify the calibration on a day-to-day basis.

Step 1--Copiously rinse the electrode with water. Immerse it in 20 mL of pH 7 buffer and stir for 1 to 2 minutes. Discard the buffer and replace with an additional 40 mL of pH 7 buffer. While the solution is gently stirred, measure the pH. Adjust the pH meter calibration knob until the pH is equal to the theoretical pH of the buffer. Record the theoretical pH and final, measured pH reading. (The two values should be identical).

Step 2--Copiously rinse the electrode with water. Immerse it in 20 mL of pH 4 QC sample and stir for 1 to 2 minutes. Discard the sample and replace with an additional 40 mL pH 4 QC sample. While the solution is stirred, measure and record the pH. From the calibration curve of pH versus pH*, determine the pH* for the observed pH. Compare pH* to the theoretical pH of the QC sample. The two values must agree within ±0.05 pH unit. If the two values do not agree, the rigorous calibration procedure (section 4.8.3.1) must be performed prior to sample analysis.

Step 3--Repeat step 2 with the pH 10 QC sample. This sample must be kept under a $CO_2$-free atmosphere when in use, or acceptable results may not be obtained.

## 4.9 Quality Control

### 4.9.1 Duplicate Analysis

Analyze one sample per batch in duplicate. The duplicate precision (expressed as an RSD) must be less than or equal to 10 percent. If the duplicate precision is unacceptable (RSD >10 percent), then a problem exists in the experimental technique. Determine and eliminate the cause of the poor precision prior to continuing sample analysis.

### 4.9.2 Blank Analysis

Determine the alkalinity in one blank per batch. The calculations are described in section 4.11.1. The absolute value of the alkalinity must be less than or equal to 10 µeq/L. If it is not, contamination is indicated. Determine and eliminate the contamination source (often the source will be the water or KCl) prior to continuing sample analysis.

### 4.9.3 pH QCCS

Prior to analysis of the first sample in a shift and every five samples thereafter, the appropriate pH QC sample (pH 4 QC for acid titrations and pH 10 QC for base titrations) must be analyzed using the following procedure. Copiously rinse the electrode with deionized water. Immerse it in 20 mL of QC sample and stir it for 30 to 60 seconds. Discard the sample and replace with an additional 40 mL of QC sample. While the solution is gently stirred, measure and record the pH. From the calibration curve of pH versus pH*, determine the pH*. If the pH* and theoretical pH of the QC sample differ by more than ±0.05 pH unit, stop the analysis and repeat the rigorous electrode calibration (Section 4.8.3.1). Previously analyzed samples (up to last acceptable QC sample) must be reanalyzed. Acceptable values of pH* are reported on Form 12.

### 4.9.4 Comparison of Initial Titration pH Values

The values for measured pH at $V_{titrant} = 0$ (before KCl spike) of the acid and base titrations should be within ±0.1 pH unit. If they are not, check operation to ensure that cross-contamination is not occurring.

For a sample with Alk $\leq -15$ µeq/L, calculate a value for alkalinity as follows:

$$[\mathrm{Alk}]_{CO} = 10^6 \times 10^{-pH^*} \text{ (pH at V = 0)}$$

(The pH at $V_{titrant} = 0$ is taken from the acid titration.) If Alk differs from $[\mathrm{Alk}]_{CO}$ by more than ±10 µeq/L then check the electrode operation and calibration.

### 4.9.5 Comparison of Calculated Alkalinity and Measured Alkalinity

A value for Alk can be calculated from a sample's DIC concentration and pH. Two sets of pH and DIC values are obtained in the lab, (1) pH* at V=0 of the base titration and the associated DIC concentration, and (2) pH of the air-equilibrated sample and the associated DIC concentration. Each set can be used to calculate a value for Alk. The calculated values for Alk can then be compared to the measured value of Alk. The comparison is useful in checking both the validity of assuming a carbonate system and the possibility of analytical error. Alk is calculated from pH and DIC as follows:

$[\mathrm{Alk}]_{C1}$ = calculated Alk from initial pH and DIC at time of base titration

$[\mathrm{Alk}]_{C2}$ = calculated Alk from air-equilibrated pH and DIC

$$[\mathrm{Alk}]_C\ (\mu eq/L) = \left[ \frac{DIC}{12{,}011} \left( \frac{[H^+]K_1 + 2\,K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2} \right) + \frac{K_w}{[H^+]} - [H^+] \right] \times 10^6$$

DIC = DIC in mg/L (the factor 12,011 converts mg/L to moles/L)
$[H^+] = 10^{-pH}$
$K_1 = 4.4463 \times 10^{-7}$ at 25°C
$K_2 = 4.6881 \times 10^{-11}$ at 25°C
$K_w = 1.0023 \times 10^{-14}$ at 25°C

$[Alk]_{C1}$ and $[Alk]_{C2}$ are compared as follows:

For $[Alk]_{C1} \leq 100$ µeq/L, the following condition applies

$$\left| [Alk]_{C1} - [Alk]_{C2} \right| \leq 15 \ \mu eq/L$$

For $[Alk]_{C1} > 100$ µeq/L, the following condition applies

$$\left| \frac{[Alk]_{C1} - [Alk]_{C2}}{([Alk]_{C1} + [Alk]_{C2})/2} \times 100 \right| \leq 10\%$$

If either of the above conditions is not satisfied, then the pH and DIC values are suspect and must be remeasured. It is very important that the pH and DIC be measured as closely together in time as possible. If they are not measured closely in time, acceptable agreement between $[Alk]_{C1}$ and $[Alk]_{C2}$ may not be obtained. When acceptable values for $[Alk]_{C1}$ and $[Alk]_{C2}$ are obtained, their average is compared to the measured Alk as described below.

For $[Alk]_{C\text{-}avg} \leq 100$ µeq/L, then the difference "D" and the acceptance window "w" are

$$D = [Alk]_{C\text{-}avg} - Alk \text{ and } w = 15 \ \mu eq/L$$

For $[Alk]_{C\text{-}avg} > 100$ µeq/L, then

$$D = \frac{[Alk]_{C\text{-}avg} - Alk}{[Alk]_{C\text{-}avg}} \times 100 \text{ and } w = 10\%$$

If $|D| \leq w$, it is valid to assume a carbonate system. If $D < -w$ then the assumption of a pure carbonate system is not valid and the sample contains noncarbonate protolytes (soluble reacting species), such as organic species. If $D > w$, then an analytical problem exists in the pH determination, DIC determination, or acid titration (such as titrant concentration). In this case the problem must be identified and the sample must be reanalyzed.

### 4.9.6 Comparison of Calculated Acidity and Measured Acidity

Just as for alkalinity, pH and DIC values can be used to calculate an Acy value. Since the Acy of a sample changes with changing DIC, only the initial pH and DIC values measured at the beginning of the base titration are used to calculate an Acy value. This calculated Acy is then compared to the measured Acy value. Acy is calculated by

$$[\mathrm{Acy}]_C\ (\mu\mathrm{eq/L}) = \left[\frac{\mathrm{DIC}}{12{,}011}\left(\frac{[\mathrm{H^+}]^2 - K_1K_2}{[\mathrm{H^+}]^2 + [\mathrm{H^+}]K_1 + K_1K_2}\right) + [\mathrm{H^+}] - \frac{K_w}{[\mathrm{H^+}]}\right] \times 10^6$$

$[\mathrm{Acy}]_C$ is compared to Acy as described below.

For $[\mathrm{Acy}]_C \leq 100$ µeq/L, then

$$D = [\mathrm{Acy}]_C - \mathrm{Acy} \text{ and } w = 10\ \mu\mathrm{eq/L}$$

For $[\mathrm{Acy}]_C > 100$ µeq/L, then

$$D = \frac{[\mathrm{Acy}]_C - \mathrm{Acy}}{[\mathrm{Acy}]_C} \times 100 \text{ and } w = 10\%$$

If $|D| \leq w$, then it is valid to assume a carbonate system. If $D < -w$, the assumption of a pure carbonate system is not valid, and the sample contains noncarbonate protolytes, such as organic species.

If $D > w$, then an analytical problem exists in the pH determination, DIC determination, or base titration (such as titrant concentration). In this case the problem must be identified and the sample must be reanalyzed.

### 4.9.7 Comparison of Calculated Total Carbonate and Measured Total Carbonate

If the assumption of a carbonate system is valid, the sum of Alk plus Acy is equal to the total carbonate. This assumption can be checked by calculating the total carbonate from the DIC, then comparing the calculated total carbonate to the measured estimate of total carbonate (the sum of Alk plus Acy). The total carbonate is calculated by

$$C_C\ (\mu\mathrm{mole/L}) = \mathrm{DIC\ (mg/L)} \times 83.26\ (\mu\mathrm{mole/mg})$$

$C_C$ is compared to (Alk + Acy) as follows:

For $C_C \leq 100$ µmole/L, then

$$D = C_C - (\mathrm{Alk} + \mathrm{Acy}) \text{ and } w = 10\ \mu\mathrm{mole/L}$$

For $C_C$ >100 µmole/L, then

$$D = \frac{C_C - (Alk + Acy)}{C_C} \times 100 \text{ and } w = 10\%$$

If $|D| \leq w$, the assumption of a carbonate system is valid. If $D < -w$, the assumption is not valid and the sample contains noncarbonate protolytes. If $D > w$, an analytical problem exists. It must be identified and the sample must be reanalyzed.

## 4.10 Procedure

An acid titration (section 4.10.1) and a base titration (section 4.10.2) are necessary to determine the acidity and alkalinity of a sample. As part of each titration, the sample pH is determined. The air-equilibrated pH is determined in a separate sample portion (section 4.10.3).

### 4.10.1 Acid Titration

Step 1--Allow a sealed water sample (aliquot 5) to reach ambient temperature.

Step 2--Copiously rinse the electrode with deionized water, then immerse in 10 to 20 mL sample. Stir for 30 to 60 seconds.

Step 3--Pipet 40.00 mL of sample into a clean, dry titration flask. Add a clean Teflon stir bar and place on a magnetic stirrer. Stir at a medium speed (no visible vortex).

Step 4--Immerse the pH electrode and read pH. Record pH on Forms 11 and 13 when the reading stabilizes (1 to 2 minutes). This is the initial measured pH at $V_{titrant} = 0$.

Step 5--Add 0.40 mL 0.1M KCl. Read and record the pH on Form 13. This is the initial measured pH at $V_{titrant} = 0$ after addition of KCl spike.

Step 6--Add increments of 0.01N HCl as specified in the table below. Record the volume of HCl added and the pH when a stable reading is obtained. Adjust the volume increment of titrant so that readings can be taken at pH values of 4.5 and 4.2. Continue the titration until the pH is between 3.3 and 3.5. Obtain at least six data points that have a pH less than 4.

| pH | Maximum Volume Increment of HCl Titrant (mL) |
|---|---|
| >9 | 0.1 |
| 7.0 to 9.0 | 0.025 |
| 5.5 to 7.0 | 0.1 |
| 4.5 to 5.5 | 0.05 |
| 3.75 to 4.50 | 0.1 |
| <3.75 | 0.3 |

### 4.10.2 Base Titration

Step 1--Take a portion of aliquot 5 at this time for DIC determination. If the DIC is not determined immediately, the sample must be kept sealed from the atmosphere. A simple way to do this is to withdraw the sample for DIC using a syringe equipped with a syringe valve. By closing the valve, the sample is sealed from the atmosphere (syringe valves that fit standard Luer-Lok syringes are available from most chromatography supply companies).

Step 2--Purge the titration vessel with $CO_2$-free air, $N_2$, or Ar.

Step 3--Copiously rinse the electrode with deionized water, then immerse in 10 to 20 mL sample for 30 to 60 seconds.

Step 4--Pipet 40.00 mL sample into the $CO_2$-free titration vessel. Maintain a $CO_2$-free atmosphere above the sample. Do not bubble the $N_2$ (or other $CO_2$-free gas) through the sample. Add a clean Teflon stir bar and place on a magnetic stirrer. Do not turn stirrer on at this point.

Step 5--Immerse the pH electrode, read pH, and record pH on Forms 11 and 13 when pH stabilizes. This is the initial measured pH at $V_{titrant} = 0$.

Step 6--Add 0.40 mL 0.10M KCl. Stir for 10 to 15 seconds. Read pH, and record pH on Form 13.

Step 7--Add 0.025 mL of 0.01N NaOH and begin gentle stirring (no visible vortex). Record the NaOH volume and pH when it stabilizes. Continue the titration by adding increments of NaOH as specified below until the pH >11. Record the volume of NaOH added and the pH after each addition. Obtain at least 10 data points in the pH region 9 to 10.5. If the initial sample pH is less than 7, obtain at least 5 data points below pH 8.

| pH | Maximum Volume Increment of NaOH Titrant (mL) |
|---|---|
| <5 | 0.025 |
| 5 to 7 | 0.050 |
| 7 to 9 | 0.025 |
| 9 to 10 | 0.10 |
| 10 to 10.5 | 0.30 |
| >10.5 | 1.00 |

### 4.10.3 Air-Equilibrated pH Measurement

Step 1--Allow the sealed sample (aliquot 5) to reach ambient temperature.

Step 2--Copiously rinse the electrode with deionized water, then immerse in 10 to 20 mL sample. Stir for 30 to 60 seconds.

Step 3--Pipet 20 to 40 mL sample into a clean, dry titration flask. Add a clean Teflon stir bar and place on a magnetic stirrer. Stir at a medium speed.

Step 4--Bubble standard gas containing 300 ppm $CO_2$ through the sample for 20 minutes. Measure and record the pH.

Step 5--Take a subsample at this time for DIC determination. The subsample must be kept sealed from the atmosphere prior to analysis. The DIC should be measured as soon as possible.

## 4.11 Calculations

During the titrations, any substance which reacts with the acid or base is titrated. However, for calculations, it is assumed that the samples represent carbonate systems and that the only reacting species are $H^+$, $OH^-$, $H_2CO_3$, $HCO_3^-$, and $CO_3^{2-}$. Using this assumption, the two parameters "Alkalinity" (Alk) and "$CO_2$-Acidity" (Acy) are calculated. The validity of the assumption is checked as described in sections 4.9.6 through 4.9.8. Note that for blank samples only the initial calculations are required (section 4.11.1).

The theory behind the calculations is available elsewhere (Kramer, 1982; Butler, 1982; Kramer, 1984). Examples of the calculations are given in Appendix C.

### 4.11.1 Initial Calculations

Step 1--From the calibration curve of measured pH versus calculated pH (pH*), determine pH* for each pH value obtained during both the acid and base titrations. Next, convert all pH* values to hydrogen ion concentrations using the equation

$$[H^+] = 10^{-pH^*}$$

Step 2--Using the acid titration data, calculate the Gran function $F_{1a}$ for each data pair ($V_a$, pH*) in which pH* <4:

$$F_{1a} = (V_s + V_a)\,[H^+]$$

$V_s$ = Total initial sample volume (40.00 + 0.400)mL
$V_a$ = Cumulative volume of acid titrant added

Step 3--Plot $F_{1a}$ versus $V_a$. The data should be on a straight line with the equation

$$F_{1a} = a + bV$$

Step 4--Perform a linear regression of $F_{1a}$ on $V_a$ to determine the correlation coefficient (r) and the coefficients a and b. The coefficient r should exceed 0.999. If it does not, examine the data to ensure that only data on the linear portion of the plot were used in the regression. If any outliers are detected, repeat the regression analysis. Calculate an initial estimate of the equivalence volume ($V_1$) by

$$V_1 = -a/b$$

Further calculations are based on this initial estimate of $V_1$ and the initial sample pH*. Table 4.1 below lists the appropriate calculation procedure for the various combinations of $V_1$ and initial sample pH*.

TABLE 4.1. LIST OF CALCULATION PROCEDURES FOR COMBINATIONS OF INITIAL $V_1$ AND pH*

| Sample Description | | Calculation Procedure | Section No. |
|---|---|---|---|
| Initial $V_1$ | Initial pH* | | |
| <0 | - | A | 4.11.2 |
| >0 | $\leq$7.6 | B | 4.11.3 |
| >0 | >7.6 | C | 4.11.4 |

NOTE: For blank analyses, calculate Alk by Alk = $V_1 C_a/V_{sa}$. Further calculations are not necessary.

Throughout the calculations, there are several equations and constants that are frequently used. These are listed in Table 4.2.

TABLE 4.2. LIST OF FREQUENTLY USED EQUATIONS AND CONSTANTS

| No. | Equation |
|---|---|
| 1 | $F_{1c} = (V_s + V)\left[\frac{C([H^+]K_1 + 2\,K_1K_2)}{[H^+]^2 + [H^+]K_1 + K_1K_2} + \frac{K_w}{[H^+]} - [H^+]\right]$ |
| 2 | $F_{2c} = (V_s + V)\left[\frac{C([H^+]^2 - K_1K_2)}{[H^+]^2 + [H^+]K_1 + K_1K_2} + [H^+] - \frac{K_w}{[H^+]}\right]$ |

Constants[a] and variable descriptions

$V_s$ = Total initial sample volume
$V$ = Cumulative volume of titrant added
$C$ = Total carbonate expressed in moles/L
$[H^+]$ = Hydrogen ion concentration
$K_1$ = $4.4463 \times 10^{-7}$ at 25°C
$K_2$ = $4.6881 \times 10^{-11}$ at 25°C
$K_w$ = $1.0023 \times 10^{-14}$ at 25°C

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[a] Constants are taken from Butler, 1982.

### 4.11.2 Calculation Procedure A (Initial $V_1 < 0$)

Step 1--From the base titration data, determine which data set (V, pH*) has the pH* nearest (but not exceeding) a pH = 8.2. As an initial estimate, set the equivalence volume $V_2$ equal to the volume of this data set. Next, calculate initial estimates of Alk, Acy, and C by

$$\text{Alk} = \frac{V_1 C_a}{V_{sa}}$$

$C_a$ = concentration of acid titrant

$V_{sa}$ = original sample volume (acid titration)

$$Acy = \frac{V_2 C_b}{V_{sb}}$$

$C_b$ = concentration of base titrant

$V_{sb}$ = original sample volume (base titration)

$C$ = total carbonate = Alk + Acy

Step 2--Calculate the Gran function $F_{1c}$ for the first 7 to 8 points of the base titration using equation 1, Table 4.2. Plot $F_{1c}$ versus $V_b$. Perform a linear regression with the points lying on the linear portion of the plot. Determine the coefficients of the line $F_{1c} = a + bV$. The coefficient r should exceed 0.999. If it does not, examine the plot to ensure that only points on the linear portion are used. From the coefficients, calculate a new estimate of $V_1$ by

$$V_1 = -a/b$$

Step 3--Calculate the Gran function $F_{2c}$ (equation 2, Table 4.2) for data from the base titration across the current estimate of $V_2$. (Use the first 4 to 6 sets with a volume less than $V_2$ and the first 6 to 8 sets greater than $V_2$.) Plot $F_{2c}$ versus $V_b$. The data should lie on a straight line with the equation $F_{2c} = a + bV$. Perform a linear regression of $F_{2c}$ on $V_b$ and determine the coefficients of the line. If $r < 0.999$ reexamine the data to ensure that only points on the linear portion were used in the regression. Calculate a new estimate of $V_2$ by

$$V_2 = -a/b$$

Step 4--Calculate new estimates of Alk, Acy, and C using the new estimates of $V_1$ and $V_2$ (an asterisk indicates a new value).

$$Alk^* = \frac{-V_1 C_b}{V_{sb}} \; ; \quad Acy^* = \frac{V_2 C_b}{V_{sb}} \; ; \quad C^* = Alk + Acy$$

Step 5--Compare the latest two values for total carbonate. If

$$\left| \frac{C - C^*}{C + C^*} \right| > 0.001$$

then calculate a new estimate for C by

$$C(\text{new}) = (C + C^*)/2$$

Step 6--Using the new value for C, repeat the calculations for the Gran functions and for new values of C. Continue repeating the calculations until the relative difference between C and C* is less than 0.001.

Step 7--When the expression is less than 0.001, convert the final values for Alk, Acy, and C to μeq/L by

$$\text{Alk } (\mu eq/L) = \text{Alk } (eq/L) \times 10^6$$

$$\text{Acy } (\mu eq/L) = \text{Acy } (eq/L) \times 10^6$$

$$C \ (\mu eq/L) = C \ (eq/L) \times 10^6$$

4.11.3 Calculation Procedure B (Initial $V_1 > 0$, Initial pH* $\leq 7.6$)

Step 1--From the base titration data, determine which data set (V, pH*) has the pH* nearest, but not exceeding, 8.2. As an initial estimate, set the equivalence volume $V_2$ equal to the volume of this data set. Next calculate initial estimates of Alk, Acy, and C by

$$\text{Alk} = \frac{V_1C_a}{V_{sa}} \ ; \quad \text{Acy} = \frac{V_2C_b}{V_{sb}} \ ; \quad C = \text{Alk} + \text{Acy}$$

Step 2--Calculate the Gran function $F_{1c}$ (equation 1) for data sets from the acid titration with volumes across the current estimate of $V_1$ (use the first 4 to 6 sets with volumes less than $V_1$ and the first 6 to 8 sets with volumes greater than $V_1$). Plot $F_{1c}$ versus $V_a$. The data should lie on a line with the equation $F_{1c} = a + bV$. Perform a linear regression of $F_{1c}$ on $V_a$ and determine the coefficients of the line.

If r does not exceed 0.999, reexamine the data to ensure that no outliers were used in the regression. Calculate a new estimate for $V_1$ by

$$V_1 = -a/b$$

Step 3--Calculate the Gran function $F_{2c}$ (equation 2) for data sets from the base titration with volumes across the current estimate of $V_2$. (Use the first 4 to 6 sets with volumes less than $V_2$ and the first 6 to 8 sets with volumes greater than $V_2$). Plot $F_{2c}$ versus $V_b$. The data should lie on a line with the equation $F_{2c} = a + bV$. Perform a linear regression of $F_{2c}$ on $V_b$ and determine the coefficients of the line. If r does not exceed 0.999, reexamine the data to ensure that only data on the linear portion were included in the regression. Calculate a new estimate for $V_2$ by

$$V_2 = -a/b$$

Step 4--Calculate new estimates of Alk, Acy, and C using the latest estimates of $V_1$ and $V_2$.

$$\text{Alk}^* = \frac{V_1C_a}{V_{sa}} \quad ; \quad \text{Acy}^* = \frac{V_2C_b}{V_{sb}} \quad ; \quad C^* = \text{Alk} + \text{Acy}$$

Step 5--Compare the latest two values for total carbonate. If

$$\left|\frac{C - C^*}{C + C^*}\right| > 0.001$$

then calculate a new estimate of C by

$$C(\text{new}) = (C + C^*)/2$$

Step 6--Using the new value of C, repeat the calculations for the Gran functions and for new values of C (steps 2 through 5). Continue repeating the calculations until the above expression is less than 0.001.

When the expression is less than 0.001, convert the final values for AlK, Acy, and C to μeq/L by

$$\begin{aligned}\text{Alk } (\mu\text{eq/L}) &= \text{Alk (eq/L)} \times 10^6\\ \text{Acy } (\mu\text{eq/L}) &= \text{Acy (eq/L)} \times 10^6\\ \text{C } (\mu\text{eq/L}) &= \text{C (eq/L)} \times 10^6\end{aligned}$$

4.11.4 Calculation Procedure C (Initial $V_1 > 0$, Initial pH* >7.6)

Step 1--Obtain an initial estimate of the equivalence volume $V_2$ by following the procedure in step 2 if the initial sample pH* $\geq$8.2. If the initial sample pH* <8.2, then follow the procedure in step 3.

Step 2--From the acid titration data, determine which data set (V, pH*) has the pH* nearest, but not exceeding, 8.2. As an initial estimate, set the equivalence volume $V_2$ equal to the volume of this data set. Go to step 4.

Step 3--Using data sets from the acid titration with pH* values across a pH = 7 (use 4 to 6 sets with a pH* $\leq$7 and 4 to 6 sets with a pH* $\geq$7), calculate the Gran function $F_{2a}$ by

$$F_{2a} = (V_1 - V_a)\,[H^+]$$

Step 4--Plot $F_{2a}$ versus $V_a$. The data should lie on a straight line with the equation $F_{2a} = a + bV$. Perform a linear regression of $F_{2a}$ on $V_a$. The coefficient r should exceed 0.999. If it does not, reexamine the plot to ensure that only data on the linear portion were used in the calculation. Calculate a new estimate for $V_2$ by

$$V_2 = -a/b$$

Step 5--Calculate estimates of Alk, Acy, and C by

$$\text{Alk} = \frac{V_1C_a}{V_{sa}} \;;\quad \text{Acy} = \frac{-V_2C_a}{V_{sa}} \;;\quad C = \text{Alk} + \text{Acy}$$

Step 6--Calculate the Gran function $F_{1c}$ (equation 1) for data sets from the acid titration with volumes across the current estimate of $V_1$ (use the first 4 to 6 sets with volumes less than $V_1$ and the first 6 to 8 sets with volumes greater than $V_1$). Plot $F_{1c}$ versus $V_a$. The data should lie on a straight line with the equation $F_{1c} = a + bV$. Perform a linear regression of $F_{1c}$ on $V_a$ and determine the coefficients of the line. The coefficient r should exceed 0.999. If it does not, reexamine the plot to ensure that only data on the linear portion were included in the regression. Calculate a new estimate for $V_1$ by

$$V_1 = -a/b$$

Step 7--Calculate the Gran function $F_{2c}$ (equation 2) for data sets from the acid titration with volumes across the current estimate of $V_2$ (use the first 4 to 6 sets with volumes less than $V_2$ and the first 6 to 8 sets with volumes greater than $V_2$). Plot $F_{2c}$ versus $V_a$. The data should lie on a straight line with the equation $F_{2c} = a + bV$. Perform a linear regression of $F_{2c}$ on $V_a$ and determine the coefficients of the line. The coefficient r should exceed 0.999. If it does not, reexamine the plot to ensure that only data on the linear portion were included in the regression. Calculate a new estimate of $V_2$ by

$$V_2 = -a/b$$

Step 8--Calculate new estimates of Alk, Acy, and C using the latest estimates of $V_1$ and $V_2$.

$$\text{Alk}^* = \frac{V_1C_a}{V_{sa}} \;;\quad \text{Acy}^* = \frac{-V_2C_a}{V_{sa}} \;;\quad C^* = \text{Alk} + \text{Acy}$$

Step 9--Compare the latest two values for total carbonate. If

$$\left|\frac{C - C^*}{C + C^*}\right| > 0.001$$

then calculate a new estimate of C by

$$C(\text{new}) = (C + C^*)/2$$

Step 10--Using this new value of C, repeat the calculations in steps 6 through 9. Continue repeating the calculations until the above expression is less than 0.001.

Step 11--When the expression is less than 0.001, convert the final values for Alk, Acy, and C to µeq/L by

$$\text{Alk } (\mu\text{eq/L}) = \text{Alk } (\text{eq/L}) \times 10^6$$
$$\text{Acy } (\mu\text{eq/L}) = \text{Acy } (\text{eq/L}) \times 10^6$$
$$\text{C } (\mu\text{eq/L}) = \text{C } (\text{eq/L}) \times 10^6$$

## 4.12 Precision and Accuracy

In a multiple lab study using 115 lake samples containing 10-1000 µeq/L alkalinity, 10-200 µeq/L acidity, and pH values in the range 4-8, the overall duplicate precision was 1.1 percent rsd, 9.0 percent rsd, and ±0.06 pH units, respectively (note that this is the overall within lab duplicate precision).

In a multiple lab study using two synthetic simulated lake samples containing 116 and 464 µeq/L ANC respectively, the percent recoveries obtained were 96 percent (n=57) and 103 percent (n=57), respectively.

## 4.13 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Butler, J. N., 1982. Carbon Dioxide Equilibria and Their Applications. Addison-Wesley Publications, Reading, Massachusetts.

Gran, G., 1952. Determination of the Equivalence Point in Potentiometric Titrations. Part II. Analyst, v. 77, pp. 661-671.

Kramer, J. R., 1982. Alkalinity and Acidity. In: R. A. Minear and L. H. Keith (eds.), Water Analysis, Vol. 1. Inorganic Species, Part 1. Academic Press, Orlando, Florida.

Kramer, J. R., 1984. Modified Gran Analysis for Acid and Base Titrations. Environmental Geochemistry Report No. 1984-2. McMaster University, Hamilton, Ontario, Canada.

McQuaker, N. R., P. D. Kluckner, and D. K. Sandberg, 1983. Chemical Analysis of Acid Precipitation: pH and Acidity Determinations. Environ. Sci. Technol., v. 17, n. 7, pp. 431-435.

National Bureau of Standards, 1982. Simulated Precipitation Reference Materials, IV. NBSIR 82-2581. U.S. Department of Commerce - NBS, Washington, D.C.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes, Method 150.1, pH. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

# 5.0 DETERMINATION OF AMMONIUM

## 5.1 Scope and Application

This method covers the determination of ammonia in natural surface waters in the range of 0.01 to 2.6 mg/L $NH_4^+$. This range is for photometric measurements made at 630 to 660 nm in a 15-mm or 50-mm tubular flow cell. Higher concentrations can be determined by sample dilution. Approximately 20 to 60 samples per hour can be analyzed.

## 5.2 Summary of Method

Alkaline phenol and hypochlorite react with ammonia to form an amount of indophenol blue that is proportional to the ammonium concentration. The blue color formed is intensified with sodium nitroprusside (U.S. EPA, 1983).

## 5.3 Interferences

Calcium and magnesium ions may be present in concentration sufficient to cause precipitation problems during analysis. A 5 percent EDTA solution is used to prevent the precipitation of calcium and magnesium ions.

Sample turbidity may interfere with this method. Turbidity is removed by filtration at the field station. Sample color that absorbs in the photometric range used also interferes.

## 5.4 Safety

The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use protective clothing (lab coat and gloves) and safety glasses when preparing reagents.

## 5.5 Apparatus and Equipment

- Technicon AutoAnalyzer Unit (AAI or AAII) consisting of sampler, manifold (AAI) or analytical cartridge (AAII), proportioning pump, heating bath with double-delay coil (AAI), colorimeter equipped with 15-mm tubular flow cell and 630- to 660-nm filters, recorder, and digital printer for AAII (optional).

## 5.6 Reagents and Consumable Materials

- Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

- Sulfuric Acid (5N), Air Scrubber Solution--Carefully add 139 mL concentrated sulfuric acid to approximately 500 mL ammonia-free water. Cool to room temperature and dilute to 1 L with water.

- Sodium Phenolate Solution--Using a 1-L Erlenmeyer flask, dissolve 83 g phenol in 500 mL water. In small increments, cautiously add with agitation 32 g NaOH. Periodically cool flask under flowing tap water. When cool, dilute to 1 L with water.

- Sodium Hypochlorite Solution--Dilute 150 mL of a bleach solution containing 5.25 percent NaOCl (such as "Clorox") to 500 mL with water. Available chlorine level should approximate 2 to 3 percent. Clorox is a proprietary product, and its formulation is subject to change. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. Due to the instability of this product, storage over an extended period should be avoided.

- Disodium Ethylenediamine-Tetraacetate (EDTA) (5 percent w/v)--Dissolve 50 g EDTA (disodium salt) and approximately six pellets NaOH in 1 L water.

- Sodium Nitroprusside (0.05 percent w/v)--Dissolve 0.5 g sodium nitroprusside in 1 L deionized water.

- $NH_4^+$ Stock Standard Solution (1,000 mg/L)--Dissolve 2.9654 g anhydrous ammonium chloride, $NH_4Cl$ (dried at 105°C for 2 hours) in water, and dilute to 1,000 mL.

- Standard Solution A (10.00 mg/L $NH_4^+$)--Dilute 10.0 mL $NH_4^+$ stock standard solution to 1,000 mL with water.

- Standard Solution B (1.000 mg/L $NH_4^+$)--Dilute 10.0 mL standard solution A to 100.0 mL with water.

Using standard solutions A and B, prepare (fresh daily) the following standards in 100-mL volumetric flasks:

| $NH_4^+$ (mg/L) | mL Standard Solution/100 mL |
|---|---|
| | Solution B |
| 0.01 | 1.0 |
| 0.02 | 2.0 |
| 0.05 | 5.0 |
| 0.10 | 10.0 |

| $NH_4^+$ (mg/L) | mL Standard Solution/100 mL |
|---|---|
| | Solution A |
| 0.20 | 2.0 |
| 0.50 | 5.0 |
| 0.80 | 8.0 |
| 1.00 | 10.0 |
| 1.50 | 15.0 |
| 2.00 | 20.0 |

## 5.7 Sample Collection, Preservation, and Storage

Samples are collected, filtered, and preserved (addition of $H_2SO_4$ until pH <2) in the field. The samples must be stored in the dark at 4°C when not in use.

## 5.8 Calibration and Standardization

Analyze the series of ammonium standards as described in Section 5.10.

Prepare a calibration curve by plotting the peak height versus standard concentration.

## 5.9 Quality Control

The required QC is described in Section 3.4.

## 5.10 Procedure

Since the intensity of the color used to quantify the concentration is pH-dependent, the acid concentration of the wash water and the standard ammonium solutions should approximate that of the samples. For example, if the samples have been preserved with 2 mL concentrated $H_2SO_4$/L, the wash water and standards should also contain 2 mL concentrated $H_2SO_4$/L.

Step 1--For a working range of 0.01 to 2.6 mg/L $NH_4^+$ (AAI), set up the manifold as shown in Figure 5.1. For a working range of 0.01 to 1.3 mg/L $NH_4^+$ (AAII), set up the manifold as shown in Figure 5.2. Higher concentrations may be accommodated by sample dilution.

Step 2--Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through sample line.

Step 3--For the AAI system, sample at a rate of 20/hr, 1:1. For the AAII use a 60/hr 6:1 cam with a common wash.

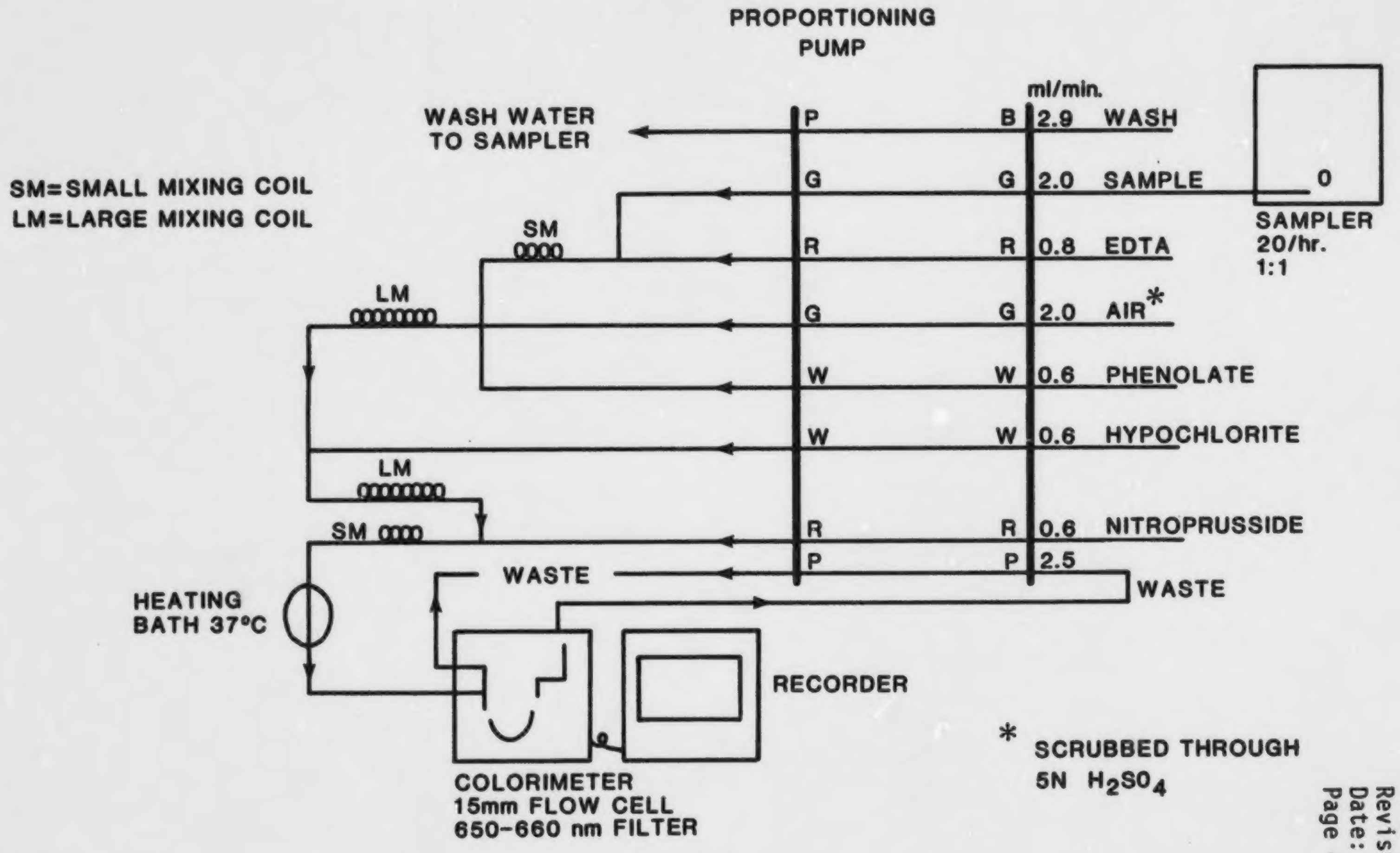
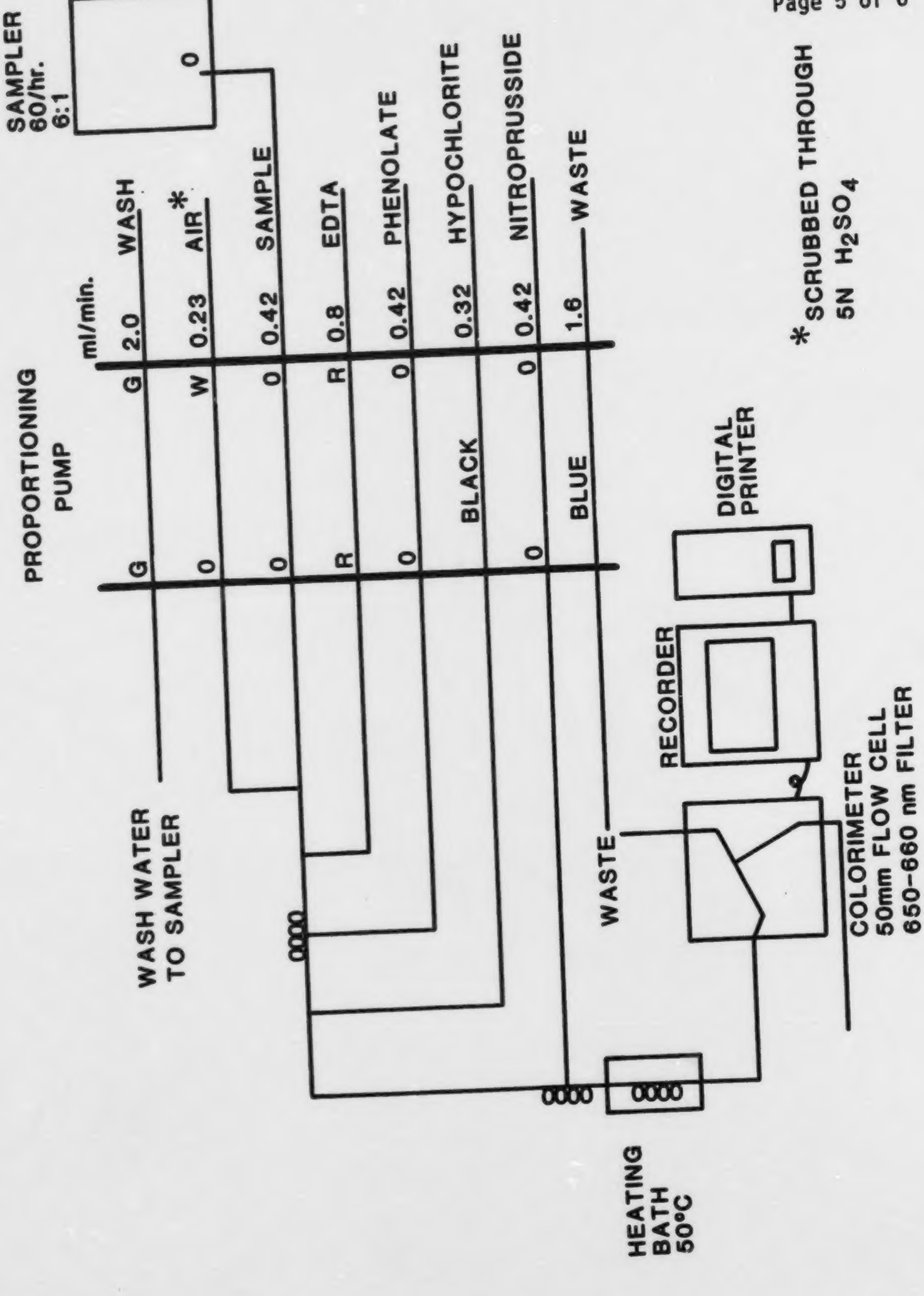

PROPORTIONING
PUMP
ml/min.
WASH WATER
TO SAMPLER
SM=SMALL MIXING COIL
LM=LARGE MIXING COIL
P
B
2.9
WASH
G
G
2.0
SAMPLE
0
SAMPLER
20/hr.
1:1
SM
R
R
0.8
EDTA
LM
G
G
2.0
AIR*
W
W
0.6
PHENOLATE
W
W
0.6
HYPOCHLORITE
LM
SM
R
R
0.6
NITROPRUSSIDE
P
P
2.5
WASTE
WASTE
HEATING
BATH 37°C
RECORDER
COLORIMETER
15mm FLOW CELL
650-660 nm FILTER
* SCRUBBED THROUGH
5N $H_2SO_4$

Figure 5.1. Ammonia manifold AAI.


SAMPLER
60/hr.
6:1
0
PROPORTIONING PUMP
ml/min.
G
G
2.0
WASH
0
W
0.23
AIR*
0
0
0.42
SAMPLE
R
R
0.8
EDTA
0
0
0.42
PHENOLATE
BLACK
0.32
HYPOCHLORITE
0
0
0.42
NITROPRUSSIDE
BLUE
1.6
WASTE
WASH WATER TO SAMPLER
0000
WASTE
DIGITAL PRINTER
RECORDER
COLORIMETER
50mm FLOW CELL
650-660 nm FILTER
0000
0000
HEATING BATH 50°C

*SCRUBBED THROUGH 5N $H_2SO_4$

Figure 5.1. Ammonia manifold AAI.

Step 4--Load sampler tray with unknown samples.

Step 5--Switch sample line from water to sampler and begin analysis.

Step 6--Dilute and reanalyze samples with an ammonia concentration exceeding the calibrated concentration range.

## 5.11 Calculations

Compute concentration of samples by comparing sample peak heights with calibration curve. Report results in mg/L $NH_4^+$.

## 5.12 Precision and Accuracy

In a single laboratory (EMSL-Cincinnati), using surface-water samples at concentrations of 1.41, 0.77, 0.59, and 0.43 mg $NH_3$-N/L, the standard deviation was ±0.005 (U.S. EPA, 1983).

In a single laboratory (EMSL-Cincinnati), using surface-water samples at concentrations of 0.16 and 1.44 mg $NH_3$-N/L, recoveries were 107 percent and 99 percent, respectively (U.S. EPA, 1983). These recoveries are statistically significantly different from 100 percent.

## 5.13 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes, Method 350.1, Ammonia Nitrogen. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

# 6.0 DETERMINATION OF CHLORIDE, NITRATE, AND SULFATE BY ION CHROMATOGRAPHY

## 6.1 Scope and Application

This method is applicable to the determination of chloride, nitrate, and sulfate in natural surface waters by ion chromatography (IC). It is restricted to use by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram.

## 6.2 Summary of Method

Samples are analyzed by IC. IC is a liquid chromatographic technique that combines ion exchange chromatography, eluent suppression, and conductimetric detection.

A filtered sample portion is injected into an ion chromatograph. The sample is pumped through a precolumn, separator column, suppressor column, and a conductivity detector. The precolumn and separator column are packed with a low-capacity anion exchange resin. The sample anions are separated in these two columns based on their affinity for the resin exchange sites.

The suppressor column reduces the conductivity of the eluent to a low level and converts the sample anions to their acid form. Typical reactions in the suppressor column are:

$$\underset{\text{(high-conductivity eluant)}}{Na^+\ HCO_3^- + R - H} \longrightarrow \underset{\text{(low conductivity)}}{H_2CO_3 + R - Na}$$

$$Na^+\ A^- + R - H \longrightarrow HA + R - Na$$

Three types of suppressor columns are available: the packed-bed suppressor, the fiber suppressor, and the micromembrane suppressor. The packed-bed suppressor contains a high-capacity cation exchange resin in The hydrogen form. It is consumed during analysis and must be periodically regenerated off-line. The latter two suppressors are based on cation exchange membranes. These suppressors are continuously regenerated throughout the analysis. Also, their dead volume is substantially less than that of a packed-bed suppressor. For these two reasons, the latter two suppressors are preferred.

The separated anions in their acid form are measured using a conductivity cell. Anion identification is based on retention time. Quantification is performed by comparing sample peak heights to a calibration curve generated from known standards (ASTM, 1984a; O'Dell et al., 1984; Topol and Ozdemir, 1981).

## 6.3 Interferences

Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. The lake samples are not expected to contain any interfering species. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution or spiking can be used to solve most interference problems.

The water dip or negative peak that elutes near, and can interfere with, the chloride peak can be eliminated by the addition of the concentrated eluant so that the eluant and sample matrix are similar.

Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in ion chromatograms.

Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

## 6.4 Safety

Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operation. The calibration standards, samples, and most reagents pose no hazard to the analyst. Protective clothing and safety glasses should be worn when handling concentrated sulfuric acid.

## 6.5 Apparatus and Equipment

- Ion Chromatograph--Analytical system complete with ion chromatograph and all accessories (conductivity detector, autosampler, data recording system, etc.).
- Anion Preseparator and Separator Columns--Dionex Series AG-4A and AS-4A are recommended for use with the 2000i ion chromatographs. AG-3 and AS-3 columns are recommended for older ion chromatographs.
- Suppressor Column--Dionex AFS fiber suppressor or AMMS membrane suppressor is recommended.

## 6.6 Reagents and Consumable Materials

Unless stated otherwise, all chemicals must be ACS reagent grade or better. Also, salts used in preparation of standards must be dried at 105°C for 2 hours and stored in a desiccator.

- Deionized Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984b).

- Eluant Solution (0.0028M $NaHCO_3$/0.0020M $Na_2CO_3$)--Dissolve 0.94 g sodium bicarbonate ($NaHCO_3$) and 0.85 g sodium carbonate ($Na_2CO_3$) in water and dilute to 4 L. This eluant strength may be adjusted for different columns according to the manufacturer's recommendations.

- Fiber Suppressor Regenerant (0.025N $H_2SO_4$)--Add 2.8 mL concentrated sulfuric acid ($H_2SO_4$, Baker Ultrex grade or equivalent) to 4 L water.

- Stock Standard Solutions--Store stock standards in clean polyethylene bottles (cleaned without acid using procedure in Appendix A) at 4°C. Prepare monthly.

    a. Bromide Stock Standard Solution (1,000 mg/L $Br^-$)--Dissolve 1.2877 g sodium bromide (NaBr) in water and dilute to 1.000 L.

    b. Chloride Stock Standard Solution (200 mg/L $Cl^-$)--Dissolve 0.3297 g sodium chloride (NaCl) in water and dilute to 1.000 L.

    c. Fluoride Stock Standard Solution (1,000 mg/L $F^-$)--Dissolve 2.2100 g sodium fluoride (NaF) in water and dilute to 1.000 L.

    d. Nitrate Stock Standard Solution (200 mg/L $NO_3^-$)--Dissolve 0.3261 g potassium nitrate ($KNO_3$) in water and dilute to 1.000 L.

    e. Phosphate Stock Standard Solution (1,000 mg/L P)--Dissolve 4.3937 g potassium phosphate ($KH_2PO_4$) in water and dilute to 1.000 L.

    f. Sulfate Stock Standard Solution (1,000 mg/L $SO_4^{2-}$)--Dissolve 1.8141 g potassium sulfate ($K_2SO_4$) in water and dilute to 1.000 L.

- Mixed Resolution Sample (1 mg/L $F^-$, 2 mg/L $Cl^-$, 2 mg/L $NO_3^-$, 2 mg/L P, 2 mg/L $Br^-$, 5 mg/L $SO_4^{2-}$)

  Prepare by appropriate mixing and dilution of the stock standard solutions.

## 6.7 Sample Collection, Preservation, and Storage

Samples are collected and filtered in the field. Store samples at 4°C when not in use.

## 6.8 Calibration and Standardization

Each day (or work shift) for each analyte, analyze a blank and a series of standards which bracket the expected analyte concentration range as described in section 6.10. Prepare the standards daily by quantitative dilution of the stock standard solutions. Suggested concentrations for the dilute standards are given in Table 6.1.

TABLE 6.1. SUGGESTED CONCENTRATION OF DILUTE CALIBRATION STANDARDS

| | Concentration (mg/L) | | |
|---|---|---|---|
| Standard | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ |
| 1 | 0 | 0 | 0 |
| 2 | 0.020 | 0.020 | 0.20 |
| 3 | 0.10 | 0.10 | 0.50 |
| 4 | 0.50 | 0.50 | 2.00 |
| 5 | 1.00 | 1.00 | 5.00 |
| 6 | 3.00 | 3.00 | 10.00 |

Prepare a calibration curve for each analyte by plotting peak height versus standard concentration.

## 6.9 Quality Control

General QC procedures are described in section 3.4.

After calibration, perform a resolution test. Analyze the mixed standard containing fluoride, chloride, nitrate, phosphate, bromide, and sulfate. Resolution between adjacent peaks must equal or exceed 60 percent. If it is not, replace or clean the separator column and repeat calibration.

## 6.10 Procedure

Step 1--Set up the IC for operation. Typical operating conditions for a Dionex 2010i IC are given in Table 6.2. Other conditions may be used depending upon the columns and system selected.

Step 2--Adjust detector range to cover the concentration range of samples.

Step 3--Load injection loop (manually or via an autosampler) with the sample (or standard) to be analyzed. Load five to ten times the volume required to thoroughly flush the sample loop. Inject the sample. Measure and record (manually or with a data system) the peak heights for each analyte.

Step 4--Dilute and reanalyze samples with an analyte concentration exceeding the calibrated concentration range.

TABLE 6.2. TYPICAL IC OPERATING CONDITIONS

IC: Dionex 2010i Sample Loop Size: 250 µL

Precolumn: AG-4A

Separator Column: AS-4A

Suppressor Column: AMMS

Eluant: 0.75mM $NaHCO_3$/2.0mM $Na_2CO_3$

Eluant Flow Rate: 2.0 mL/min

Regenerant: 0.025N $H_2SO_4$

Regenerant Flow Rate: 3 mL/min

| Ion | Typical Retention Time (min) |
|---|---|
| $Cl^-$ | 1.8 |
| $NO_3^-$ | 4.9 |
| $SO_4^{2-}$ | 8.1 |

6.11 Calculations

Compute the sample concentration by comparing the sample peak height with the calibration curve. Report results in mg/L.

6.12 Precision and Accuracy

Typical single operator results for surface water analyses are listed in Table 6.3 (O'Dell et al., 1984).

TABLE 6.3. SINGLE-OPERATOR ACCURACY AND PRECISION (O'Dell et al., 1984)[a]

| Ion | Spike (mg/L) | Number of Replicates | Mean % Recovery | Standard Deviation (mg/L) |
|---|---|---|---|---|
| $Cl^-$ | 1.0 | 7 | 105 | 0.14 |
| $NO_3^-$ | 0.5 | 7 | 100 | 0.0058 |
| $SO_4^{2-}$ | 10.0 | 7 | 112 | 0.71 |

[a] The chromatographic conditions used by O'Dell were slightly different than those listed in Table 6.2. However, the results are typical of what is expected.

## 6.13 References

American Society for Testing and Materials, 1984a. Annual Book of ASTM Standards, Vol. 11.01, Standard Test Method for Anions in Water by Ion Chromatography, D4327-84. ASTM, Philadelphia, Pennsylvania.

American Society for Testing and Materials, 1984b. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

O'Dell, J. W., J. D. Pfaff, M. E. Gales, and G. D. McKee, 1984. Technical Addition to Methods for the Chemical Analysis of Water and Wastes, Method 300.0, The Determination of Inorganic Anions in Water by Ion Chromatography. EPA-600/4-85-017. U.S. Environmental Protection Agency, Cincinnati, Ohio.

Topol, L. E., and S. Ozdemir, 1984. Quality Assurance Handbook for Air Pollution Measurement Systems: Vol. V. Manual for Precipitation Measurement Systems, Part II. Operations and Maintenance Manual. EPA-600/4-82-042b. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

# 7.0 DETERMINATION OF DISSOLVED ORGANIC CARBON AND DISSOLVED INORGANIC CARBON

## 7.1 Scope and Application

This method is applicable to the determination of DIC and DOC in natural surface waters, and it is written assuming that a Dohrman-Xertex DC-80 Analyzer is used. However, any instrumentation having similar operating characteristics may also be used.

The method is applicable over the concentration range 0.1 to 30 mg/L DIC or DOC. The method detection limit is about 0.8 mg/L DOC and 0.1 mg/L DIC, as determined from replicate analyses of a blank sample.

## 7.2 Summary of Method

Two samples, aliquots 4 and 5, are sent to the lab for analysis. Aliquot 4 is filtered and preserved in the field (acidified to pH <2 with $H_2SO_4$). It is analyzed for DOC. Aliquot 5 is an unfiltered sample. It is filtered and analyzed for DIC.

DOC is determined (after external sparging to remove DIC) by ultraviolet-promoted persulfate oxidation, followed by IR detection. DIC is determined directly by acidifying to generate $CO_2$ followed by IR detection (U.S. EPA, 1983; Xertex-Dohrman, 1984).

## 7.3 Interferences

No interferences are known.

## 7.4 Safety

The sample types, standards, and most reagents pose no hazard to the analyst. Protective clothing (lab coat) and safety glasses should be worn when preparing reagents and operating the instrument.

## 7.5 Apparatus and Equipment

- Disposable plastic Luer-Lok syringes (for DIC samples) equipped with Luer-Lok syringe valves.
- Carbon Analyzer--This method is based on the Dohrman DC-80 Carbon Analyzer equipped with a high-sensitivity sampler. The essential components of the instrument are a sample injection valve, UV-reaction chamber, IR detector, and integrator. The injection valve should have a 5- to 7-mL sample loop and should permit injection with a standard Luer-Lok syringe. Other instruments having similar performance characteristics may also be used.

- Reagent Bottle for Standard Storage--Heavy-wall borosilicate glass bottle with three two-way valves in the cap. Suitable suppliers include (but are not limited to) Rainin Instrument Co. (Catalog No. 45-3200) and Anspec Co. (Catalog No. H8332).

## 7.6 Reagents and Consumable Materials

- DOC Calibration Stock Solution (2,000 mg/L DOC)--Dissolve 0.4250 g potassium hydrogen phthalate (KHP, primary standard grade, dried at 105°C for 2 hours) in water, add 0.10 mL phosphoric acid (ACS reagent grade), and dilute to 100.00 mL with water. Store in an amber bottle at 4°C. Prepare monthly.

- Dilute Daily DOC Calibration Solutions--Using micropipets and volumetric pipets, prepare the following calibration standards daily.

  a. 0.500 mg/L DOC - dilute 0.125 mL DOC stock solution plus 0.5 mL phosphoric acid to 500.00 mL with water.
  b. 1.000 mg/L DOC - dilute 0.250 mL DOC stock solution plus 0.5 mL phosphoric acid to 500.00 mL with water.
  c. 5.000 mg/L DOC - dilute 1.250 mL DOC stock solution plus 0.5 mL phosphoric acid to 500.00 mL with water.
  d. 10.00 mg/L DOC - dilute 2.500 mL DOC stock solution plus 0.5 mL phosphoric acid to 500.00 mL with water.
  e. 30.00 mg/L DOC - dilute 3.750 mL DOC stock solution plus 0.25 mL phosphoric acid to 250.00 mL with water.

  Store in amber bottles at 4°C.

- DOC QC Stock Solution (1,000 mg/L DOC)--Dissolve 0.5313 g KHP in water, add 0.25 mL phosphoric acid, then dilute to 250.00 mL with water. Store in an amber bottle at 4°C. The QC stock solution must be prepared using an independent source of KHP. Prepare monthly.

- Dilute Daily DOC QC Solutions--Prepare the following QC samples daily.

  a. 0.500 mg/L DOC (Detection Limit QC Sample - DL QCCS) - dilute 0.250 mL QC stock solution plus 0.5 mL phosphoric acid to 500.00 mL with water.
  b. 10.00 mg/L DOC - dilute 2.500 mL QC stock solution plus 0.25 mL phosphoric acid to 250.00 mL with water.
  c. 30.00 mg/L DOC - dilute 3.000 mL QC stock solution plus 0.1 mL phosphoric acid to 100.00 mL with water.

  Store in amber bottles at 4°C.

- DIC Calibration Stock Solution (2,000 mg/L DIC)--Dissolve 4.4131 g sodium carbonate ($Na_2CO_3$, primary standard grade, freshly dried at 105°C for 2 hours) in water and dilute to 250.00 mL with water. Store in a tightly capped bottle under a $CO_2$-free atmosphere. Prepare weekly.

- Dilute DIC Calibration Solutions--Prepare the following calibration standards daily. Store in tightly capped bottles under a $CO_2$-free atmosphere.

  a. 0.500 mg/L DIC - dilute 0.250 mL DIC stock solution to 1.000 L with water.
  b. 1.000 mg/L DIC - dilute 0.250 mL DIC stock solution to 500.00 mL with water.
  c. 5.000 mg/L DIC - dilute 1.250 mL DIC stock solution to 500.00 mL with water.
  d. 10.00 mg/L DIC - dilute 2.500 mL DIC stock solution to 500.00 mL with water.
  f. 30.00 mg/L DIC - dilute 3.750 mL DIC stock solution to 250.00 mL with water.

- DIC QC Stock Solution (1,000 mg/L DIC)--Dissolve 2.2065 g $Na_2CO_3$ in water and dilute to 250.00 mL with water. Store in a tightly capped bottle under a $CO_2$-free atmosphere. The QC stock solution must be prepared using an independent source of $Na_2CO_3$.

- Dilute DIC QC Solutions--Prepare the following QC samples daily.

  a. 0.500 mg/L DIC (Detection Limit QC Sample - DL QCCS) - dilute 0.250 mL QC stock solution to 500.00 mL with water.
  b. 10.00 mg/L DIC - dilute 2.500 mL QC stock solution to 250.00 mL with water.
  c. 30.00 mg/L DIC - dilute 3.000 mL QC stock solution to 100.00 mL with water.

- Potassium Persulfate Reagent (2 percent w/v)--Dissolve 20 g potassium persulfate ($K_2S_2O_8$, ACS reagent grade or better) in water, add 2.0 mL phosphoric acid, then dilute to 1.0 L with water. This reagent is used for DOC analyses.

- Phosphoric Acid Reagent (5 percent v/v)--Dilute 50.0 mL concentrated phosphoric acid (ACS reagent grade) to 1.0 L with water. This reagent is used for DIC analyses.

- Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

## 7.7 Sample Collection, Preservation, and Storage

The sample for DOC analysis (aliquot 4) is collected, filtered, and preserved in the field (pH adjusted to less than 2 with sulfuric acid). Store at 4°C when not in use.

The sample for DIC analysis (aliquot 5) is collected in the field and is not filtered or preserved. Store at 4°C and minimize atmospheric exposure.

## 7.8 Calibration and Standardization

### 7.8.1 DOC Calibration

7.8.1.1 Set-up--Set up the instrument according to the manufacturer's instructions. Adjust all liquid and gas flow rates. Turn on UV lamp and allow the system to stabilize. The IR detector must warm up for at least 2 hours. For best results, leave the IR detector on at all times.

7.8.1.2 Routine Calibration--For the range of interest (0 to 30 mg/L DOC) the instrument is designed to be calibrated with a single 10.00 mg/L DOC standard. The linearity of the calibration is checked with the QC samples. If acceptable results are not obtained for the QC samples, the instrument must be calibrated using the procedure in section 7.8.1.3.

Step 1--Sparge the 10.00-mg/L calibration standard for 5 to 6 minutes with $CO_2$-free gas.

Step 2--Following the instructions in the operating manual, calibrate the instrument using three replicate analyses of the 10.00-mg/L standard.

Step 3--Analyze a system blank and a reagent blank. Both must contain less than 0.1 mg/L DOC. If either contains more DOC, then the water is contaminated. In this case, all standards and reagents must be prepared again with DOC-free water, and the instrument must be recalibrated.

Step 4--After sparging for 5 to 6 minutes, analyze the 0.500, 10.00, and 30.00 mg/L QC samples. Acceptable results are 0.50 ± 0.10, 10.0 ± 0.5, and 30.0 ± 1.5 mg/L, respectively. If acceptable results are not obtained for all QC samples, the instrument calibration is inadequate (nonlinear). In this case, recalibrate the instrument using the procedure in section 7.8.1.3.

7.8.1.3 Nonroutine Calibration--If the inherent instrument calibration procedure is inadequate (nonlinear over the range of interest), then the instrument must be calibrated manually. This is done by analyzing a series of calibration standards and generating a calibration curve by plotting instrument response versus standard concentration. Sample concentrations are then determined by inverse interpolation. The procedure is outlined in steps 1 through 5.

Step 1--Sparge the 0.500, 1.000, 5.000, 10.00, and 30.00 mg/L DOC calibration standard for 5 to 6 minutes with $CO_2$-free gas.

Step 2--Erase the instrument calibration (if present). Analyze each standard and record the uncalibrated response.

Step 3--Plot the response versus standard concentration. Draw or calculate (using linear regression) the best calibration curve.

Step 4--Analyze a system blank and a reagent blank. From their response and the calibration curve determine their concentrations. Both must contain less than 0.1 mg/L DOC. If either contains more than 0.1 mg/L DOC, then the water is contaminated. In this case, the standards and reagents must be prepared again using DOC-free water, and the instrument must be recalibrated.

Step 5--After sparging for 5 to 6 minutes, analyze the 0.500 and 10.00 mg/L QC samples. From their response and the calibration curve, determine the concentration of each QC sample. Acceptable results are 0.5 ± 0.1 and 10.0 ± 0.5 mg/L, respectively. If unacceptable results are obtained, the calibration standards must be prepared again and reanalyzed. Acceptable results must be obtained prior to sample analysis.

### 7.8.2 DIC Calibration

7.8.2.1 Set-up--Set up the instrument according to the manfacturer's instructions. Adjust all liquid and gas flow rates, using 5 percent phosphoric acid as the reagent. Do not turn on the UV lamp. Allow the system to stabilize.

7.8.2.2 Routine Calibration--The calibration procedure is identical to that for DOC (section 7.8.1.2) with the exception that the DIC standards are not sparged prior to analysis.

7.8.2.3 Nonroutine Calibration--The nonroutine calibration procedure is identical to that for DOC (section 7.8.1.3) with the exception that the DIC standards are not sparged prior to analysis.

## 7.9 Quality Control

In addition to the QC inherent in the calibration procedures (section 7.8), the QC procedures described in section 3.4 must be performed.

## 7.10 Procedure

### 7.10.1 DOC Analysis

Step 1--Calibrate the carbon analyzer for DOC.

Step 2--Sparge samples with $CO_2$-free gas for 5 to 6 minutes (sparge gas should have a flow of 100 to 200 cc/min). Load and analyze the sample as directed by the instrument operating manual.

### 7.10.2 DIC Analysis

NOTE: For QA reasons, it is very important that the DIC is measured at the same time pH is measured (section 4).

Calibrate the carbon analyzer for DIC.

7.10.2.1 Routine Determination--Rinse a clean syringe with sample. Withdraw a fresh sample portion into the syringe. Attach a syringe filter (0.45 µm) and simultaneously filter the sample and inject it into the carbon analyzer. Analyze as directed by the instrument operating manual.

7.10.2.2 Air-Equilibrated Determination--As described in section 4.10.3, equilibrate the sample with 300 ppm $CO_2$ in air. Rinse a clean syringe with the air-equilibrated sample. Withdraw a fresh portion of the air-equilibrated sample and attach a syringe filter (0.45 µm). Simultaneously filter and inject the sample into the carbon analyzer. Analyze as directed by the instrument operating manual.

## 7.11 Calculations

If the routine calibration procedure is satisfactory, the instrument outputs the sample results directly in mg/L. DOC or DIC calculations are not necessary.

If a calibration curve is necessary, determine the sample concentration by comparing the sample response to the calibration curve. Report results as mg/L DOC or DIC.

## 7.12 Precision and Accuracy

### 7.12.1 DOC

In a single laboratory (EMSL-Cincinnati), using raw river water, centrifuged river water, drinking water, and the effluent from a carbon column which had concentrations of 3.11, 3.10, 1.79, and 0.07 mg/L total organic carbon respectively, the standard deviations from 10 replicates were 0.13, 0.03, 0.02, and 0.02 mg/L, respectively (U.S. EPA, 1983).

In a single laboratory (EMSL-Cincinnati), using potassium hydrogen phthalate in distilled water at concentrations between 5.0 and 1.0 mg/L total organic carbon, recoveries were 80 percent and 91 percent, respectively (U.S. EPA, 1983).

### 7.12.2 DIC

In a multiple lab study using two lake samples containing 0.42 and 9.9 mg/L DIC respectively, the relative standard deviations were 19 percent (n=41) and 5.2 percent (n=7), respectively.

In a single laboratory (EMSL-Las Vegas), using sodium carbonate in deionized water at concentrations of 0.150, 0.500, 2.00, and 30.00 mg/L DIC, recoveries were 94, 101, 100, and 98 percent, respectively.

## 7.13 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes, Method 415.2, Organic Carbon, Total (low level) (UV promoted, persulfate oxidation). EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

Xertex-Dohrman Corporation, 1984. DC-80 Automated Laboratory Total Organic Carbon Analyzer Systems Manual, 6th Ed. Xertex-Dohrman, Santa Clara, California.

# 8.0 DETERMINATION OF TOTAL DISSOLVED FLUORIDE BY ION-SELECTIVE ELECTRODE

## 8.1 Scope and Application

This method is applicable to the determination of total dissolved fluoride in natural surface waters, using a fluoride ion-selective electrode (ISE). The applicable concentration range is 0.005 to 2 mg/L fluoride ($F^-$).

## 8.2 Summary of Method

The total dissolved fluoride in a sample is determined electrometrically using a fluoride ion-selective electrode, after addition to the sample of a total ionic strength buffer solution (TISAB). The TISAB adjusts sample ionic strength and pH and breaks up fluoride complexes.

The potential of the fluoride ISE varies logarithmically as a function of the fluoride concentration. A calibration curve is prepared by measuring the potential of known fluoride standards (after TISAB addition) and plotting the potential versus fluoride concentration (on a semi-log scale). Sample concentrations are determined by comparing the sample potential to the calibration curve.

This method is based on existing methods (U.S. EPA, 1983; Barnard and Nordstrom, 1982; Bauman, 1971; LaZerte, 1984; Kissa, 1983; Warner and Bressan, 1973).

## 8.3 Interferences

The electrode potential is partially a function of temperature. As a result, standards and samples must be equilibrated to the same temperature (±1°C).

The sample pH must be in the range 5 to 7 to avoid complexation of fluoride by hydronium (pH <5) and hydroxide (pH >7). The addition of TISAB to samples and standards ensures that the pH is maintained in the correct range.

Polyvalent cations may interfere by complexing fluoride, thereby preventing detection by the electrode. The TISAB solution contains a decomplexing agent to avoid potential interferences from polyvalent cations.

Fluoride is ubiquitous. Good laboratory practices and extra care must be used in order to minimize contamination of samples and standards.

## 8.4 Safety

The sample types, calibration standards, and most reagents pose no hazard to the analyst. Protective clothing (lab coat and gloves) and safety glasses must be worn when handling concentrated sodium hydroxide.

## 8.5 Apparatus and Equipment

- Digital electrometer (pH/mV meter) with expanded mV scale capable of reading 0.1 mV
- Combination Reference - Fluoride ion selective electrode
- Thermally isolated magnetic stirrer and Teflon-coated stir bar

## 8.6 Reagents and Consumable Materials

Unless otherwise specified, all chemicals must be ACS reagent grade or better. Use only plasticware (cleaned as described in Appendix A) for reagent preparation.

- TISAB Solution--To approximately 500 mL water in a 1-L beaker, add 57 mL glacial acetic acid (Baker Ultrex grade or equivalent), 4 g CDTA*, and 58 g sodium chloride (NaCl, ultrapure). Stir to dissolve, and cool to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with 5N NaOH (about 150 mL will be required). Transfer the solution to a 1 L volumetric flask and dilute to the mark with water. Transfer to a clean polyethylene (LPE) bottle. (Note: Alternatively, commercially available TISAB solution may be used.)
- Sodium Hydroxide Solution (5N NaOH)--Dissolve 200 g NaOH in water, cool, then dilute to 1 L. Store in a tightly sealed LPE bottle.
- Fluoride Calibration Solutions
  a. Concentrated Fluoride Calibration Stock Solution (1,000 mg/L $F^-$)--Dissolve 0.2210 g of sodium fluoride (NaF, ultrapure, dried at 110°C for 2 hours and stored in a desiccator) in water and dilute to 100.00 mL. Store in a clean LPE bottle.
  b. Dilute Fluoride Calibration Stock Solution (10.00 mg/L $F^-$)--Dilute 1.000 mL of the concentrated fluoride calibration stock solution to 100.00 mL with water.
  c. Dilute Fluoride Working Standards--Using micropipets and volumetric pipets, prepare daily a series of dilute working standards in the

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*1,2-cyclohexylene dinitrilo tetraacetic acid.

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range 0.0-2 mg/L F$^-$ by quantitatively diluting appropriate volumes of the 10.00 mg/L F$^-$ solution and TISAB solution to 50.00 mL. The following series may be used:

| mL of TISAB | mL of 10.00 mg/L F$^-$ Solution | Resulting F$^-$ Concentration When Diluted to 50.00 mL (mg/L) |
|---|---|---|
| 5.00 | 0.000 | 0.0000 |
| 5.00 | 0.0500 | 0.0100 |
| 5.00 | 0.100 | 0.0200 |
| 5.00 | 0.250 | 0.0500 |
| 5.00 | 0.500 | 0.100 |
| 5.00 | 2.50 | 0.500 |
| 5.00 | 10.00 | 2.000 |

- Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

## 8.7 Sample Collection, Preservation, and Storage

Samples are collected and filtered in the field and are shipped to the lab in LPE bottles. Store at 4°C when not in use.

## 8.8 Calibration and Standardization

Step 1--Allow the electrometer to warm up, and ensure that the fluoride-ISE contains adequate internal filling solution.

Step 2--With the electrometer set to measure mV, analyze the dilute fluoride working standards (in order of increasing concentration, beginning with the blank), using the procedure described in steps 3 through 5.

Step 3--Prior to use and between determinations, rinse the electrode with water until a potential of at least 200 mV is obtained. Blot dry to avoid carryover.

Step 4--Place 20.00 mL of standard in a clean 30-mL plastic beaker. Add a clean Teflon-coated stir bar, place on a magnetic stirrer, and stir at medium speed.

Step 5--Immerse the electrode in the solution to just above the stir bar and observe the potential. Record the potential when a stable reading is obtained (potential drift less than 0.1 mV/minute). Record the time required to obtain the reading. (It may take 15 to 30 minutes to obtain a stable reading for the low standards.)

Step 6--Prepare a calibration curve on semi-logarithmic graph paper. Plot the concentration of F$^-$ (in mg/L) on the log axis versus the electrode potential on the linear axis. Determine the slope of the line in the linear portion of the plot. The measured slope should be within ±10 percent of the theoretical slope (obtained from the electrode manual). If it is not, the electrode is not operating properly. Consult the electrode manual for guidance. (Note: The calibration curve may be nonlinear below 0.05 mg/L.)

## 8.9 Quality Control

The required QC procedures are described in Section 3.4.

## 8.10 Procedure

NOTE: Use only plasticware when performing fluoride determinations. Clean using the acid-free washing procedure described in Appendix A.

Step 1--Allow samples and standards to equilibrate at room temperature.

Step 2--Analyze fluoride standards and prepare calibration curve as described in section 8.8.

Step 3--Prior to use and between determinations, rinse the electrode with water until a potential of at least 200 mV is obtained. Blot dry to avoid carryover.

Step 4--Place 10.00 mL of sample in a clean 30-mL plastic beaker. Add a clean Teflon-coated stir bar, place on a magnetic stirrer, and stir at a medium speed. Add 1.00 mL of TISAB to beaker. Record the reading when a stable potential is obtained (drift is less than 0.1 mV/minute). Also record the time required to reach the stable reading. (It may take as much as 15 to 30 minutes.) This assists the analyst in detecting electrode problems.

Step 5--At the end of the day, thoroughly rinse the electrode and store it in deionized water.

## 8.11 Calculations

Compute the sample concentration by comparing the sample potential reading to the calibration curve. Report results in mg/L.

## 8.12 Precision and Accuracy

A synthetic sample containing 0.85 mg/L fluoride and no interferences was analyzed by 111 analyst; the mean result was 0.84 mg/L and the standard deviation was 0.03 mg/L (U.S. EPA, 1983).

A synthetic sample containing 0.75 mg/L fluoride, 2.5 mg/L polyphosphate, and 300 mg/L alkalinity was analyzed by 111 analysts; the mean result was 0.75 mg/L fluoride and the standard deviation was 0.036 (U.S. EPA, 1983).

## 8.13 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Barnard, W. R., and D. K. Nordstrom, 1982. Fluoride in Precipitation - I. Methodology with the Fluoride-Selective Electrode. Atmos. Environ., v. 16, pp. 99-103.

Bauman, E. W., 1971. Sensitivity of the Fluoride-Selective Electrode Below the Micromolar Range. Anal. Chim. Acta, v. 54, pp. 189-197.

Kissa, E., 1983. Determination of Fluoride at Low Concentrations with the Ion-Selective Electrode. Anal. Chem., v. 55, pp. 1445-1448.

LaZerte, B. D., 1984. Forms of Aqueous Aluminum in Acidified Catchments of Central Ontario: A Methodological Analysis. Can. J. Fish Aquat. Sci., v. 41, n. 5, pp. 766-776.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes, Method 340.2, Fluoride (Potentiometric, Ion Selective Electrode). EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

Warner, T. B., and D. J. Bressan, 1973. Direct Measurement of Less Than 1 Part-Per-Billion Fluoride in Rain, Fog, and Aerosols with an Ion-Selective Electrode. Anal. Chim. Acta, v. 63, pp. 165-173.

# 9.0 DETERMINATION OF TOTAL PHOSPHORUS

## 9.1 Scope and Application

This method may be used to determine concentrations of total phosphorus in natural surface waters in the range from 0.001 to 0.200 mg/L P.

Samples preserved with $HgCl_2$ should not be analyzed using this method.

## 9.2 Summary of Method

All forms of phosphorus, including organic phosphorus, are converted to orthophosphate by an acid-persulfate digestion.

Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid, which upon reduction with ascorbic acid produces an intensely colored blue complex. Antimony potassium tartrate is added to increase the rate of reduction (Skougstad et al., 1979; Gales et al., 1966; Murphy and Riley, 1962).

## 9.3 Interferences

Barium, lead, and silver interfere by forming a precipitate. There is a positive interference from silica when the silica-to-total-phosphorus ratio exceeds about 400:1 (Table 9.1).

TABLE 9.1. PERCENT RECOVERY OF TOTAL P IN THE PRESENCE OF $SiO_2$
(Skougstad et al., 1979)

| | $SiO_2$ (mg/L) | | | | |
|---|---|---|---|---|---|
| Total P mg/L | 20 | 15 | 10 | 5 | 1 |
| 0.200 | 98 | 100 | 100 | 102 | 101 |
| 0.100 | 103 | --- | --- | --- | 103 |
| 0.050 | 104 | 104 | 102 | 102 | 102 |
| 0.010 | 144 | 133 | 122 | 111 | 100 |
| 0.005 | 160 | 140 | 120 | 120 | 100 |
| 0.002 | 550 | 350 | 250 | 250 | 100 |

$HgCl_2$-NaCl-preserved samples give inconsistent results and therefore should not be used.

## 9.4 Safety

The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use protective clothing (lab coat and gloves) and safety glasses when handling concentrated sulfuric acid.

Use proper care when operating the autoclave. Follow manufacturer's safety precautions.

## 9.5 Apparatus and Equipment

- Autoclave
- Technicon AutoAnalyzer II, consisting of sampler, cartridge manifold, proportioning pump, heating bath, colorimeter, voltage stabilizer, recorder, and printer With this equipment the following operating conditions have been found satisfactory for the range from 0.001 to 0.200 mg/L P:

  Absorption cell--50 mm
  Wavelength--880 nm
  Cam--30/h (1:1)
  Heating bath temperature--37.5°C.

- Glass tubes with plastic caps, disposable--18 mm by 150 mm.

## 9.6 Reagents and Consumable Materials

All reagents must be ACS reagent grade or equivalent.

- Ammonium Molybdate Solution (35.6 g/L)--Dissolve 40 g ammonium molybdate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$ in 800 mL water and dilute to 1 L.
- Ascorbic Acid Solution (18 g/L)--Dissolve 18 g ascorbic acid ($C_6H_8O_4$) in 800 mL water and dilute to 1 L.
- Antimony Potassium Tartrate Solution (3 g/L)--Dissolve 3.0 g antimony potassium tartrate $[K(SbO)C_4H_4O_6\cdot 1/2H_2O]$ in 800 mL water and dilute to 1 L.
- Combined Working Reagent--Combine reagents in the order listed below. (This reagent is stable for about 8 hours. The stability is increased if kept at 4°C):

| | |
|---|---|
| 50 mL | Sulfuric acid, 2.45M |
| 15 mL | Ammonium molybdate solution |
| 30 mL | Ascorbic acid solution |
| 5 mL | Antimony potassium tartrate solution |

- Phosphate Stock Standard Solution (100 mg/L P)--Dissolve 0.4394 g potassium acid phosphate ($KH_2PO_4$, dried for 12 to 16 hours over concentrated $H_2SO_4$, sp gr 1.84) in water and dilute to 1,000 mL.

- Phosphate Standard Solution I (10.00 mg/L P)--Quantitatively dilute 100.0 mL phosphate stock standard solution to 1,000 mL with water.

- Phosphate Standard Solution II (1.000 mg/L P)--Quantitatively dilute 10.00 mL phosphate stock standard solution to 1,000 mL with water.

- Dilute Phosphate Working Standards--Prepare a blank and 1,000 mL each of a series of working standards by appropriate quantitative dilution of phosphate standard solutions I and II. For example:

| Phosphate standard solution II (mL) | Phosphate standard solution I (mL) | Total P concentration in working standard (mg/L) |
|---|---|---|
| 0.0 | 0.0 | 0.000 |
| 1.00 | - | 0.001 |
| 5.00 | - | 0.005 |
| 10.00 | - | 0.010 |
| - | 5.0 | 0.050 |
| - | 10.0 | 0.100 |
| - | 20.0 | 0.200 |

- Potassium Persulfate Solution (4 g/L)--Dissolve 4.0 g potassium persulfate ($K_2S_2O_8$) in water and dilute to 1 L.

- Sulfuric Acid (2.45M)--Slowly, and with constant stirring and cooling, add 136 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL water. Cool, and dilute to 1 L with water.

- Sulfuric Acid (0.45M)--Slowly, and with constant stirring and cooling, add 25.2 mL concentrated sulfuric acid (sp gr 1.84) to 800 mL water. Cool, and dilute to 1 L with water.

- Sulfuric Acid-Persulfate Reagent, (1 + 1)--Mix equal volumes of 0.45M sulfuric acid and potassium persulfate solution.

- Water Diluent--Add 1.0 mL Levor IV to 1 L water.

- Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

## 9.7 Sample Collection, Preservation, and Storage

Samples are collected and preserved in the field (addition of $H_2SO_4$ until the pH <2). Store samples at 4°C when not in use.

## 9.8 Calibration and Standardization

Analyze the series of total P standards as described in section 9.10.

Prepare a calibration curve by plotting the peak height versus standard concentration.

## 9.9 Quality Control

The required QC is described in Section 3.4.

## 9.10 Procedure

NOTE: It is critical that the colorimeter is optically peaked prior to first analysis.

Step 1--Mix each sample, pipet a volume of it containing less than 0.002 mg total P (10.0 mL maximum) into a disposable glass tube, and adjust the volume to 10.0 mL.

Step 2--Prepare blank solution and sufficient standards, and adjust the volume of each to 10.0 mL.

Step 3--Add 4.0 mL acid-persulfate reagent to samples, blank, and standards.

Step 4--Place plastic caps gently on top of tubes but do not push down. Autoclave for 30 minutes at 15 psi pressure and 121°C. After the samples have cooled, the caps may be pushed down.

Step 5--Set up manifold as shown in Figure 9.1.

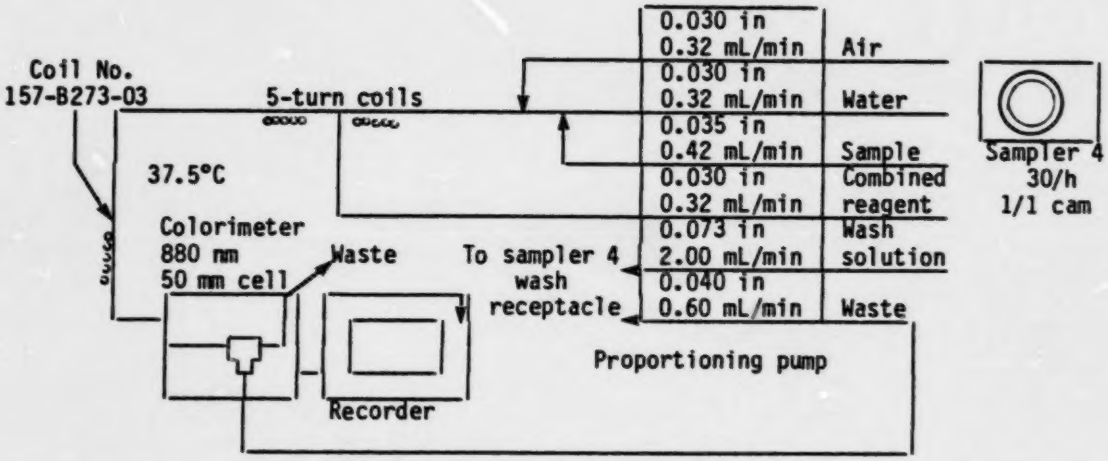
0.030 in
0.32 mL/min
Air
Coil No.
157-B273-03
0.030 in
0.32 mL/min
5-turn coils
Water
0.035 in
0.42 mL/min
Sample
Sampler 4
30/h
1/1 cam
37.5°C
0.030 in
0.32 mL/min
Combined
reagent
Colorimeter
880 nm
50 mm cell
Waste
To sampler 4
wash
receptacle
0.073 in
2.00 mL/min
Wash
solution
0.040 in
0.60 mL/min
Waste
Proportioning pump
Recorder

Figure 9.1. Total Phosphorus Manifold.

Step 6--Allow the colorimeter, recorder, and heating bath to warm up for at least 30 minutes or until the temperature of the heating bath reaches 37.5°C. Zero the recorder baseline while pumping all reagents through the system.

Step 7--Beginning with the most concentrated standard, place a complete set of standards in the first positions of the first sample tray, with blank solution between each standard. Fill remainder of each tray alternately with unknown samples and blank solution.

Step 8--Begin analysis. When the peak from the most concentrated standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale. Using the baseline control, adjust each blank in the tray to read zero as it is analyzed.

Step 9--Dilute and reanalyze samples with a total P concentration exceeding the calibrated range.

## 9.11 Calculations

Compute the concentration of total P in each sample by comparing its peak height to the calibration curve. Report results as mg/L P.

## 9.12 Precision and Accuracy

Data for the determination of the precision and accuracy of the method are given in Tables 9.2 and 9.3.

It is estimated that the RSD (coefficient of variation) of this method is 38 percent at 0.001 mg/L, 2.5 percent at 0.020 mg/L, and 2.2 percent at 0.144 mg/L.

TABLE 9.2. PRECISION OF THE METHOD FOR NATURAL WATER SAMPLES (Skougstad et al., 1979). (All data in mg/L P)

| Sample | n | Mean | Std. Dev. | Rel. Std. Dev. (%) |
|---|---|---|---|---|
| 4-065070 | 10 | 0.0347 | 0.0012 | 3.34 |
| 4-065080 | 10 | 0.1435 | 0.0031 | 2.16 |
| 4-066060 | 10 | 0.0902 | 0.0027 | 2.99 |

TABLE 9.3. PRECISION AND ACCURACY OF THE METHOD FOR ANALYST-PREPARED STANDARDS (Skougstad et al., 1979). (All data in mg/L P)

| Sample | n | Mean | Std. Dev. | Rel. Std. Dev. (%) |
|---|---|---|---|---|
| 0.040 | 9 | 0.0424 | 0.0007 | 1.71 |
| 0.030 | 10 | 0.0322 | 0.0006 | 1.96 |
| 0.020 | 10 | 0.0172 | 0.0004 | 2.45 |
| 0.004 | 9 | 0.0033 | 0.0007 | 21.21 |
| 0.001 | 9 | 0.0013 | 0.0005 | 37.5 |

## 9.13 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Gales, M. E., Jr., E. C. Julian, and R. C. Kroner, 1966. Method for Quantitative Determination of Total Phosphorus in Water. J. Am. Water Works Assoc., v. 58, pp. 1363-1368.

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Skougstad, M. W., M. J. Fishman, L. C. Friedman, D. E. Erdman, and S. S. Duncan (eds.), 1979. Method I-4600-78, Automated Phosphomolybdate Colorimetric Method for Total Phosphorus. In: Methods for Determination of Inorganic Substances in Water and Fluvial Sediments: Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A1. U.S. Government Printing Office, Washington, D.C.

# 10.0 DETERMINATION OF DISSOLVED SILICA

## 10.1 Scope and Application

This method is applicable for the determination of dissolved silica in natural surface waters in the concentration range from 0.1 to 10 mg/L.

## 10.2 Summary of Method

The procedure specified utilizes automated technology and is based on existing methodology (Skougstad et al., 1979).

Silica reacts with molybdate reagent in acid media to form a yellow silicomolybdate complex. This complex is reduced by ascorbic acid to form the molybdate blue color. The silicomolybdate complex may form either as an alpha or beta polymorph, or as a mixture of both. Because the two polymorphic forms have absorbance maxima at different wavelengths, the pH of the mixture is kept below 2.5, a condition which favors formation of the beta polymorph (Govett, 1961; Mullen and Riley, 1955; Strickland, 1962).

A 1-hour digestion with 1.0M NaOH is required to ensure that all the silica is available for reaction with the molybdate reagent.

## 10.3 Interferences

Interference from phosphate, which forms a phosphomolybdate complex, is suppressed by the addition of oxalic acid. Hydrogen sulfide must be removed by boiling the acidified sample prior to analysis. Large amounts of iron interfere. However, neither hydrogen sulfide nor iron is expected in appreciable quantities.

## 10.4 Safety

The calibration standards, samples, and most reagents used in this method pose no hazard to the analyst. Use protective clothing (lab coat and gloves) and safety glasses when handling concentrated sulfuric acid and performing sample digestions.

## 10.5 Apparatus and Equipment

- Technicon AutoAnalyzer II consisting of sampler, cartridge manifold, proportioning pump, colorimeter, voltage stabilizer, recorder, and printer.

  With this equipment the following operating conditions are recommended:

  Absorption cell--15 mm

Wavelength--660 nm
Cam 60/hour--(6/1)

## 10.6 Reagents and Consumable Materials

- Ammonium Molybdate Solution (9.4 g/L)--Dissolve 10 g ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) in 0.05M $H_2SO_4$ and dilute to 1 L with 0.05M $H_2SO_4$. Filter and store in an amber plastic container.
- Ascorbic Acid Solution (17.6 g/L)--Dissolve 17.6 g ascorbic acid ($C_6H_8O_6$) in 500 mL water containing 50 mL acetone. Dilute to 1 L with water. Add 0.5 mL Levor IV solution. The solution is stable for 1 week if stored at 4°C.
- Hydrochloric Acid (50 percent v/v)--Slowly add 500 mL concentrated HCl to 500 mL water.
- Hydrochloric Acid (2 percent v/v)--Add 10 mL (concentrated) HCl to 490 mL water.
- Hydrofluoric Acid (HF, ACS reagent grade)
- Levor IV Solution--Technicon No. 21-0332 or equivalent.
- Oxalic Acid Solution (50 g/L)--Dissolve 50 g oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) in water and dilute to 1 L.
- Silica Standard Solution (500 mg/L $SiO_2$)--Dissolve 2.366 g sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) in water and dilute to 1.000 L. The concentration of this solution must be verified by standard gravimetric analysis (described in section 10.8.1). Store in a plastic bottle.
- Silica Working Standards--Prepare a blank and 500 mL each of a series of silica working standards by appropriate quantitative dilution of the silica stock standard solution. The following series is suggested:

| Silica stock standard solution (mL) | Silica concentration in working standard (mg/L) |
|---|---|
| 0.0 | 0 |
| 0.200 | 0.200 |
| 0.500 | 0.500 |
| 1.00 | 1.00 |
| 5.00 | 5.00 |
| 10.0 | 10.0 |

- Sodium Hydroxide Solution (1.0M NaOH)--Dissolve 4 g sodium hydroxide (NaOH) in water and dilute to 1 L.

- Sulfuric Acid Solution (0.05M $H_2SO_4$) (50% v/v $H_2SO_4$)--Cautiously add 2.8 mL concentrated sulfuric acid ($H_2SO_4$, sp gr 1.84) to water and dilute to 1 L for 0.05M $H_2SO_4$. Cautiously and slowly add 500 mL $H_2SO_4$ to 500 mL water. Beware of excessive heat buildup.

- Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

## 10.7 Sample Collection, Preservation, and Storage

Samples are collected and filtered in the field, then shipped to the lab. Store at 4°C when not in use.

## 10.8 Calibration and Standardization

Verify the concentration of the silica stock standard solution using the gravimetric procedure detailed in steps 1 through 7 (APHA, 1980).

Step 1--Sample Evaporation: Add 5 mL of 50 percent v/v HCl to 200.0 mL silica stock standard. Evaporate to dryness in a 200-mL platinum evaporating dish, in several portions if necessary, on a water bath or suspended on an asbestos ring over a hot plate. Protect against contamination by atmospheric dust. During evaporation, add a total of 15 mL 50 percent HCl in several portions. Evaporate sample to dryness and place dish with residue in a 110°C oven or over a hot plate to bake for 30 minutes.

Step 2--First Filtration: Add 5 mL of 50 percent HCl, warm, and add 50 mL hot water. While hot, filter sample through an ashless medium-texture filter paper, decanting as much liquid as possible. Wash dish and residue with hot 2 percent HCl and then with a minimum volume of water, until washings are chloride-free. Save all washings. Set aside filter paper with its residue.

Step 3--Second Filtration: Evaporate filtrate and washings from the above operations to dryness in the original platinum dish. Bake residue in a 110°C oven or over a hot plate for 30 minutes. Repeat steps in section 10.8.1.2. Use a separate filter paper and a rubber policeman to aid in transferring residue from dish to filter.

Step 4--Ignition: Transfer the two filter papers and residues to a covered platinum crucible, dry at 110°C, and ignite at 1,200°C to constant weight. Avoid mechanical loss of residue when first charring and burning off the paper. Cool in desiccator, weigh, and repeat ignition and weighing until constant weight is attained. Record weight of crucible and contents.

Step 5--Volatilization with HF: Thoroughly moisten weighed residue with water. Add 4 drops of 50 percent v/v $H_2SO_4$ followed by 10 mL concentrated HF, measuring the latter in a plastic graduated cylinder or pouring an estimated 10 mL directly from the reagent bottle. Slowly evaporate to dryness over an air bath or hot plate in a hood, and avoid loss by splattering. Ignite crucible to constant weight at 1,200°C. Record weight of crucible and contents.

Step 6--Blank: Repeat steps 1 through 5 with a blank sample.

Step 7--Perform the following calculations for both the standard and blank samples.

X = weight of crucible plus contents before HF treatment (mg)
Y = weight of crucible plus contents after HF treatment (mg)

Z = weight of silica in sample (mg) = X - Y

Step 8--Calculate the silica concentration in the stock standard by:

$$\frac{\text{mg } SiO_2}{\text{L}} = \frac{\text{Z (standard) - Z (blank) mg}}{0.200 \text{ L}}$$

Step 9--Analyze the series of silica standards as described in section 10.10 (including digestion).

Step 10--Prepare a calibration curve by plotting the peak height versus standard concentration.

## 10.9 Quality Control

The required QC is described in section 3.4.

## 10.10 Procedure

Step 1--Set up the AutoAnalyzer manifold (Figure 10.1).

Step 2--Allow colorimeter and recorder to warm up for at least 30 minutes. Zero the recorder baseline while pumping all reagents through the system.

Step 3--Add 5.00 mL of 1.0M NaOH to 50.00 mL of sample. Digest for one hour.

Step 4--Beginning with the most concentrated working standard, place a complete set of standards in the first positions of the first sample tray, followed by a blank. Fill remainder of each sample tray with unknown and QC samples.

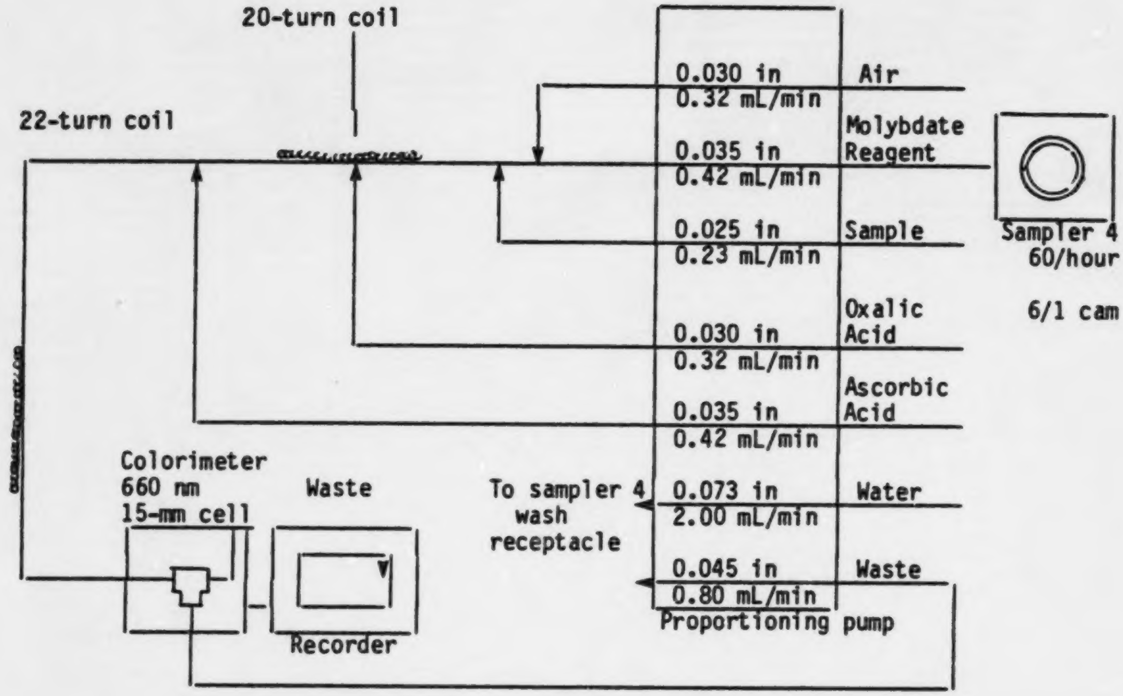
20-turn coil
22-turn coil
0.030 in
0.32 mL/min
Air
Molybdate Reagent
0.035 in
0.42 mL/min
Sample
0.025 in
0.23 mL/min
Sampler 4
60/hour
6/1 cam
Oxalic Acid
0.030 in
0.32 mL/min
Ascorbic Acid
0.035 in
0.42 mL/min
Colorimeter
660 nm
15-mm cell
Waste
To sampler 4 wash receptacle
0.073 in
2.00 mL/min
Water
0.045 in
0.80 mL/min
Waste
Proportioning pump
Recorder

Figure 10.1. Silica manifold.

Step 5--Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD CAL control until the flat portion of the curve reads full scale.

Step 6--Dilute and reanalyze any sample with a concentration exceeding the calibrated range.

## 10.11 Calculations

Compute the silica concentration of each sample by comparing its peak height to the calibration curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak. Report results as mg/L $SiO_2$.

## 10.12 Precision and Accuracy

In a multiple lab study using 111 lake samples containing 0.05-10 mg/L $SiO_2$ the duplicate relative standard deviation was 1.6 percent (note that this is the overall within-lab precision).

In a multiple lab study using two synthetic, simulated lake samples containing 10.7 and 1.07 mg/L $SiO_2$ respectively, recoveries obtained were 88 (n=21) and 95 (n=21) percent, respectively.

## 10.13 References

American Public Health Association, American Water Works Association, and Water Pollution Control Foundation, 1980. Standard Methods for the Examination of Water and Wastewater, 15th Ed. Part 425-Silica. APHA, Washington, D.C.

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

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## 11.0 DETERMINATION OF SPECIFIC CONDUCTANCE

### 11.1 Scope and Application

This method is applicable to natural surface waters of low ionic strength.

The majority of lakes sampled for the NSWS have a specific conductance in the range 10 to 100 µS/cm.

### 11.2 Summary of Method

The specific conductance in samples is measured using a conductance meter and conductivity cell. The meter and cell are calibrated using potassium chloride standards of known specific conductance (U.S. EPA, 1983).

Samples are preferably analyzed at 25°C. If they cannot be analyzed at 25°C, temperature corrections are made and results are reported at 25°C.

### 11.3 Interferences

Temperature variations represent the major source of potential error in specific conductance determinations. To minimize this error, calibration standards and samples must be measured at the same temperature.

Natural surface waters contain substances (humic and fulvic acids, suspended solids, etc.) which may build up on the conductivity cell. Such a buildup interferes with the operation of the cell and must be removed periodically, following the cell manufacturer's recommendations.

### 11.4 Safety

The calibration standards and sample types pose no hazard to the analyst.

### 11.5 Apparatus and Equipment

- Specific Conductance Meter--Digital meter with the following minimum specifications:

  Range--0.1 to 1000 µS/cm
  Readability--0.1 µS/cm
  Maximum Error--1% of reading
  Maximum Imprecision--1% of reading

- Conductivity Cell--High quality glass cell with a cell constant of 1.0 or 0.1. Cells containing platinized electrodes are recommended.

- Thermometer--NBS-traceable thermometer with a range of 0 to 40°C and divisions of 0.1°C.

## 11.6 Reagents and Consumable Materials

- Potassium Chloride Stock Calibration Solution (0.01000M KCl)--Dissolve 0.7456 g potassium chloride (KCl, ultrapure, freshly dried for two hours at 105°C and stored in a desiccator) in water and dilute to 1.000 L. Store in a tightly sealed LPE container.

- Potassium Chloride Calibration Solution (0.001000M KCl)--Dilute 10.00 mL KCl stock calibration solution to 100.00 mL with water. This solution has a theoretical specific conductance of 147.0 µS/cm at 25°C.

- Potassium Chloride QC Solution (0.000500M KCl)--Dilute 5.00 mL 0.0100M KCl solution (independent of the KCl stock calibration solution) to 100.00 mL with water. This solution has a theoretical specific conductance of 73.9 µS/cm at 25°C.

- Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

## 11.7 Sample Collection, Preservation, and Storage

The samples are collected in the field and shipped to the lab in LPE bottles without treatment. Store at 4°C when not in use.

## 11.8 Calibration and Standardization

Step 1--Measure and record the specific conductance of the KCl calibration solution as described in section 11.10.

Step 2--Calculate the corrected cell constant, $K_c$, using the following equation:

$$K_c = \frac{147.0\ \mu S/cm}{KCl_m}$$

$KCl_m$ = measured specific conductance for the KCl calibration solution.

The corrected cell constant, $K_c$, includes the calculation for the cell constant and the temperature correction to 25°C.

## 11.9 Quality Control

The required QC procedures are described in section 3.4.

## 11.10 Procedure

Step 1--Follow the manufacturer's instructions for the operation of the meter and cell.

Step 2--Allow the samples and calibration standard to equilibrate to room temperature.

Step 3--Measure the sample temperature. If different from the standard temperature, allow more time for equilibration.

Step 4--Rinse the cell thoroughly with water.

Step 5--Rinse the cell with a portion of the sample to be measured. Immerse the electrode in a fresh portion of sample and measure its specific conductance.

Step 6--Rinse the cell thoroughly with water after use. Store in water.

If the readings become erractic, the cell may be dirty or need replatinizing. Consult the manufacturer's operating manual for guidance.

## 11.11 Calculations

Calculate the corrected specific conductance ($S_c$) for each sample using the following equation:

$$S_c = (K_c)\ (S_m)$$

$K_c$ = corrected cell constant

$S_m$ = measured specific conductance

Report the results as specific conductance, µS/cm at 25°C.

## 11.12 Precision and Accuracy

Forty-one analysts in seventeen laboratories analyzed six synthetic samples contianing increments of inorganic salts, with the following results (U.S. EPA, 1983):

| Increment, as Specific Conductance (μS/cm) | Precision, as Standard Deviations (μS/cm) | Accuracy, as | |
|---|---|---|---|
| | | Bias (%) | Bias (μS/cm) |
| 100 | 7.55 | -2.02 | -2.0 |
| 106 | 8.14 | -0.76 | -0.8 |
| 808 | 66.1 | -3.63 | -29.3 |
| 848 | 79.6 | -4.54 | -38.5 |
| 1,640 | 106 | -5.36 | -87.9 |
| 1,710 | 119 | -5.08 | -86.9 |

In a single laboratory (EMSL-Cincinnati) using surface-water samples with an average conductivity of 536 μS/cm at 25°C, the standard deviation was 6 μS/cm (U.S. EPA, 1983).

## 11.13 References

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes, Method 120.1, Conductance. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

# 12.0 DETERMINATION OF METALS (Al, Ca, Fe, K, Mg, Mn, Na) BY ATOMIC ABSORPTION SPECTROSCOPY

## 12.1 Scope and Application

Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to the determination of Al, Ca, Fe, K, Mg, Mn, and Na in natural surface waters.

Detection limits, sensitivity, and optimum ranges of the metals vary with the makes and models of atomic absorption spectrophotometers. The data listed in Table 12.1, however, provide some indication of the actual concentration ranges measurable by direct aspiration (flame) and furnace techniques. In the majority of instances the concentration range shown in the table for analysis by direct aspiration may be extended much lower with scale expansion and, conversely, extended upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and through solvent extraction techniques. Lower concentrations may also be determined using the furnace techniques. The concentration ranges given in Table 12.1 are somewhat dependent on equipment such as the type of spectrophotometer and furnace accessory, the energy source, and the degree of electrical expansion of the output signal. When using furnace techniques, however, the analyst should be cautioned that chemical reactions may occur at elevated temperatures, which may result in either suppression or enhancement of the signal from the element being analyzed. To ensure valid data, the analyst must examine each matrix for interference effects (matrix spike analysis) and, if detected, must analyze the samples by the method of standard additions.

## 12.2 Summary of Method

In direct aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp, whose cathode is made of the element to be determined, is directed through the flame into a monochromator and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms are vaporized

TABLE 12.1. ATOMIC ABSORPTION CONCENTRATION RANGES[1]

| Metal | Flame: Detection Limit (mg/L) | Flame: Sensitivity (mg/L) | Flame: Optimum Concentration Range (mg/L) | Furnace[2,3]: Detection Limit (µg/L) | Furnace[2,3]: Optimum Concentration Range (µg/L) |
|---|---|---|---|---|---|
| Aluminum | 0.1 | 1 | 5 to 50 | 3 | 20 to 200 |
| Calcium | 0.01 | 0.08 | 0.2 to 7 | - | - |
| Iron | 0.03 | 0.12 | 0.3 to 5 | 1 | 5 to 100 |
| Magnesium | 0.001 | 0.007 | 0.02 to 0.5 | - | - |
| Manganese | 0.01 | 0.05 | 0.1 to 3 | 0.2 | 1 to 30 |
| Potassium | 0.01 | 0.04 | 0.1 to 2 | - | - |
| Sodium | 0.002 | 0.015 | 0.03 to 1 | - | |

[1] The concentrations shown are obtainable with any satisfactory atomic absorption spectrophotometer.

[2] For furnace sensitivity values, consult instrument operating manual.

[3] The listed furnace values are those expected when using a 20-µL injection and normal gas flow, except in the case of arsenic and selenium where gas interrupt is used.

and dissociated for absorption in the tube than the flame, the use of small sample volumes or detection of low concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor.

The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

Dissolved metals (Ca, Fe, K, Mg, Mn, and Na) are determined in a filtered sample (aliquot 1) by flame atomic absorption spectroscopy (U.S. EPA, 1983).

Total Al is determined in an unfiltered sample (aliquot 7) after digestion by graphite furnace atomic absorption spectroscopy (U.S. EPA, 1983).

Total extractable Al is determined in a sample that has been treated with 8-hydroxyquinoline and has been extracted into MIBK (aliquot 2) by graphite furnace atomic absorption spectroscopy (Barnes, 1975; May et al., 1979; Driscoll, 1984).

## 12.3 Definitions

- Optimum Concentration Range--This is a range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.
- Sensitivity--Sensitivity is the concentration in milligrams of metal per liter that produces an absorption of 1 percent.
- Dissolved Metals--Dissolved metals are those constituents (metals) which can pass through a 0.45-µm membrane filter.
- Total Metals--The concentration of metals is determined on an unfiltered sample following vigorous digestion.

## 12.4 Interferences

### 12.4.1 Direct Aspiration

The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in the magnesium and calcium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

Chemical interferences may also be eliminated by separating the metal from the interfering material. While complexing agents are primarily employed to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess of an easily ionized element.

Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multi-element lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting, and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

### 12.4.2 Flameless Atomization

Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. It is this effect which must be determined and taken into consideration in the analysis of each different matrix encountered. To verify the absence of matrix or chemical interference, a matrix spike sample is analyzed using the following procedure. Withdraw from the sample two equal aliquots. To one of the aliquots add a known amount of analyte and dilute both aliquots to the same predetermined volume. (The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4 while keeping in mind the optimum concentration range of the analysis. Under no circumstances should the dilution be less than 1:1). The diluted aliquots should then be analyzed and the unspiked results multiplied by the dilution factor should be compared to the original determination. Agreement of the results (within ±10 percent) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard helps confirm the finding from the dilution analysis. Those samples which indicate the presence of interference must be analyzed by the method of standard additions.

Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, either the use of background correction or choosing an alternate wavelength outside the absorption band should eliminate this interference. Background correction can also compensate for nonspecific broad-band absorption interference.

Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the element being analyzed.

The chemical environment of the furnace may cause certain elements to form carbides at high temperatures. This problem is greatly reduced and the sensitivity is increased with the use of pyrolytically coated graphite.

## 12.5 Safety

The calibration standards, sample types, and most reagents pose no hazard to the analyst. Use protective clothing (lab coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated hydrochloric acid, ammonium hydroxide solutions, and MIBK should be restricted to a hood.

Follow the manufacturer's safety precautions when operating the atomic absorption spectrophotometers.

Follow good laboratory practices when handling compressed gases.

## 12.6 Apparatus and Equipment

- Atomic Absorption Spectrophotometer--The spectrophotometer used shall be a single- or dual-channel, single-or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip chart recorder.
- Burner--The burner recommended by the particular instrument manufacturer should be used. For certain elements, the nitrous oxide burner is required.
- Hollow Cathode Lamps--Single element lamps are preferred, but multi-element lamps may be used. Electrodeless discharge lamps may also be used when available.
- Graphite Furnace--Any furnace device capable of reaching the specified temperatures is satisfactory.
- Strip Chart Recorder--A recorder is strongly recommended for furnace work so that there will be a permanent record and any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can be easily recognized.

## 12.7 Reagents and Consumable Materials

General reagents used in each metal determination are listed in this section. Reagents specific to particular metal determinations are listed in the particular procedure description for that metal.

- Concentrated Hydrochloric Acid (12M HCl)--Ultrapure grade (Baker Instra-Analyzed or equivalent) is required.
- HCl (1 percent v/v)--Add 5 mL concentrated HCl to 495 mL water.
- Nitric Acid (0.5% v/v $HNO_3$ - Ultrapure grade, Baker Instra-Analyzed or equivalent)--Carefully dilute $HNO_3$ in water in the ratio of 0.5 to 100.
- Stock Standard Metal Solutions--Prepare as directed in the individual metal procedures. Commercially available stock standard solutions may also be used.
- Dilute Calibration Standards--Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.
- Fuel and Oxidant--Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.
- Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

## 12.8 Sample Collection, Preservation, and Storage

Samples are collected and processed in the field. The sample for dissolved metals (aliquot 1) is filtered through a 0.45-µm membrane filter then preserved by acidifying to a pH <2 with nitric acid. The sample for total Al analysis (aliquot 7) is preserved by acidifying to a pH <2 with nitric acid. The sample for total extractable Al (aliquot 2) is prepared by mixing a portion of sample with 8-hydroxyquinoline followed by extraction with MIBK.

After processing, the samples are shipped to the analytical laboratory. For aliquot 2 samples, it is the MIBK layer from the extraction that is shipped.

## 12.9 Calibration and Standardization

The calibration procedure varies slightly with the various atomic absorption instruments.

For each analyte, calibrate the atomic absorption instrument by analyzing a calibration blank and a series of standards, following the instructions in the instrument operating manual.

The concentration of standards should bracket the expected sample concentration. However, the linear range of the instrument should not be exceeded.

When indicated by the matrix spike analysis, the analytes must be quantified by the method of standard additions. In this method, equal volumes of sample are added to a deionized water blank and to three standards containing different known amounts of the test element. The volume of the blank and of each standard must be the same. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of intersection of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 12.1. The method of standard additions can be very useful; however, for the results to be valid the following limitations must be taken into consideration:

- The absorbance plot of sample and standards must be linear over the concentration range of concern. For best results, the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20 percent) caution should be exercised.
- The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.
- The determination must be free of spectral interference and corrected for nonspecific background interference.

## 12.10 Quality Control

The required QC procedures are described in section 3.4.

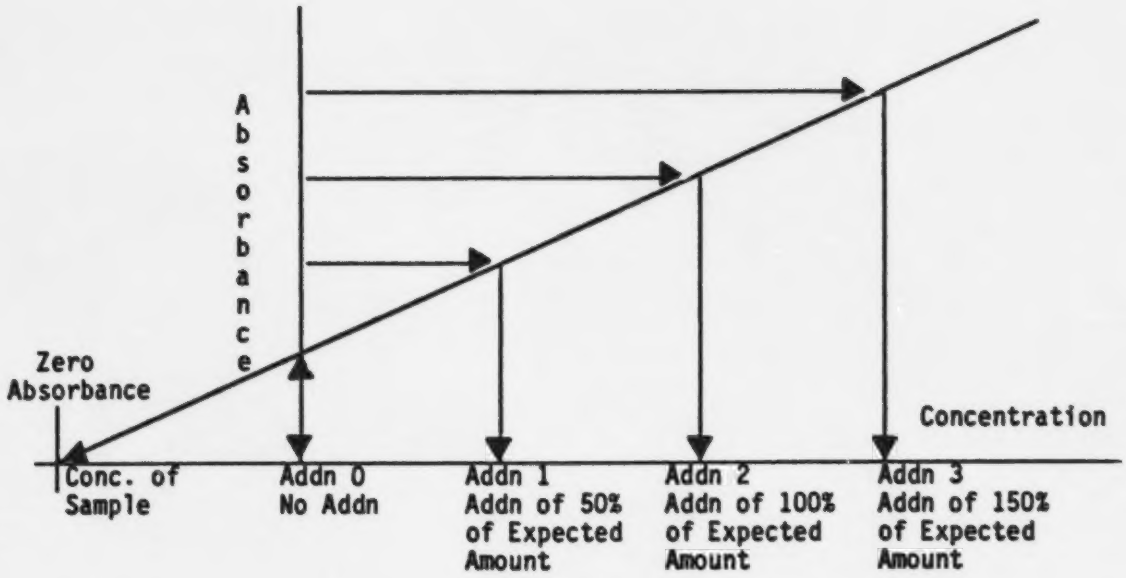

Figure 12.1. Standard Addition Plot.

## 12.11 Procedure

General procedures for flame and furnace atomic absorption analysis are given in sections 12.11.1 and 12.11.2. Detailed procedures for determining Al, Ca, Fe, K, Mg, Mn, and Na are given in sections 12.11.3 through 12.11.10.

### 12.11.1 Flame Atomic Absorption Spectroscopy

Differences among the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for his particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, the lamp should be allowed to warm up for a minimum of 15 minutes unless operated in a double-beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the element under analysis and calibrate the instrument. Aspirate the samples and determine the concentrations either directly (if the instrument reads directly in concentration units) or from the calibration curve.

### 12.11.2 Furnace Atomic Absorption Spectroscopy

Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences among various makes and models of satisfactory instruments, no detailed operating instuctions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of his particular instrument and use as a guide the temperature settings and other instrument conditions listed in sections 12.11.3 through 12.11.10 (which are the recommended ones for the Perkin-Elmer HGA-2100). In addition, the following points may be helpful.

With flameless atomization, background correction becomes of high importance, especially below 350 nm. This is because certain samples, when atomized, may absorb or scatter light from the hollow cathode lamp. These effects can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high.

If during atomization all the analyte is not volatilized and removed from the furnace, memory effects will occur. This condition is dependent on several factors, such as the volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. If this situation is detected through blank burns, the tube should be cleaned by operating the furnace at full power for the required time period at regular intervals in the analytical scheme.

Some of the smaller size furnace devices, or newer furnaces equipped with feedback temperature control (Instrumentation Laboratories MODEL 555, Perkin-Elmer MODELS HGA 2200 and HGA 76B, and Varian MODEL CRA-90) employing faster rates of atomization, can be operated using lower atomization temperatures for shorter time periods than those listed in this manual.

Although prior digestion of the sample in many cases is not required providing a representative aliquot of sample can be pipeted into the furnace, it provides for a more uniform matrix and possibly lessens matrix effects.

Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and should be reanalyzed. The use of multiple injections can improve accuracy and can help detect furnace pipetting errors.

### 12.11.3 Procedure for Determination of Total Aluminum

To determine total aluminum, a portion of sample is digested and digestate is analyzed for aluminum by furnace atomic absorption spectroscopy (U.S. EPA, 1983).

12.11.3.1 Preparation of Aluminum Standard Solutions--Aluminum stock solution (1000 mg/L Al)--Carefully weigh 1.000 gram aluminum metal (analytical reagent grade). Add 15 mL concentrated HCl and 5 mL concentrated $HNO_3$ to the metal, cover the beaker, and warm gently. When metal is completely dissolved, transfer solution quantitatively to a 1-L volumetric flask and bring to volume with water. Alternatively, a commercially available, certified Al standard may be used.

Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."

The calibration standard should be prepared in 0.5 percent (v/v) $HNO_3$.

12.11.3.2 Sample Preparation--The sample must be digested prior to analysis. Due to the low concentrations of analyte expected, contamination from atmospheric sources can be a major problem. To avoid contamination, all preparations must be performed in a laminar flow hood.

Quantitatively transfer a 50.00 mL aliquot of the well-mixed sample to a Griffin beaker. Add 3.0 mL of concentrated nitric acid. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. (DO NOT BAKE.) Allow the beaker to cool, then again add 3.0 mL of concentrated nitric acid. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate until a gentle reflux action occurs. Continue refluxing, adding acid as necessary, until the digestion is complete (indicated by a light-colored residue or no change in appearance with continued refluxing). When complete, evaporate to near dryness. Allow to cool. Add 0.5 mL of 50 percent nitric acid and warm slightly to dissolve any precipate or residue resulting from evaporation. Wash down the beaker walls and watch glass with water. Quantitatively filter the sample (to remove silicates and other insoluble materials) and adjust to 50.00 mL. The sample is now ready for analysis.

12.11.3.3 Suggested Instrument Conditions (General)

- Drying time and temperature--30 seconds at 125°C
- Ashing time and temperature--30 seconds at 1300°C
- Atomizing time and temperature--10 seconds at 2700°C
- Purge gas atmosphere--Argon
- Wavelength--309.3 nm

Other operating conditions should be set as specified by the particular instrument manufacturer.

NOTE 1: The above instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 μL injection, continuous-flow purge gas, and nonpyrolytic graphite.

NOTE 2: Background correction may be required if the sample contains a high level of dissolved solids.

NOTE 3: It has been reported that chloride ion and that nitrogen used as a purge gas suppress the aluminum signal. Therefore, the use of halide acids and nitrogen as a purge gas should be avoided.

NOTE 4: The ashing temperature can be increased to 1,500 to 1,700°C by adding 30 µg magnesium nitrate ($Mg(NO_3)_2$) (Manning et al., 1982).

NOTE 5: If blanks indicate that sample contamination is occuring, the use of Teflon labware is recommended.

12.11.3.4 Analysis Procedure

Step 1--Calibrate the instrument as directed by the instrument manufacturer.

Step 2--Analyze the samples (including required QC samples).

Step 3--If a sample concentration exceeds the linear range, dilute (with acidic media) and reanalyze.

Report results as mg/L Al.

12.11.3.5 Precision and Accuracy--In a multiple lab study using 84 lake samples containing 0.03-5 mg/L Al the overall duplicate relative standard deviation was 10.5 percent (note that this represents the overall within lab precision).

In a multiple lab study using synthetic, simulated lake samples containing 0.02 and 0.19 mg/L Al respectively, recoveries of 115 (n=21) and 103 (n=21) precent were obtained.

12.11.4 Procedure for Determination of Total Extractable Aluminum

Samples for extractable aluminum are prepared in the field and are obtained as the 8-hydroxyquinoline complex in MIBK. The MIBK solution is analyzed for aluminum by graphite furnace atomic absorption (GFAA) (Barnes, 1975; May et al., 1979; Driscoll, 1984).

12.11.4.1 Preparation of Reagents

- Glacial acetic acid (HOAc, 18M)--Baker Ultrex grade or equivalent.
- Ammonium hydroxide ($NH_4OH$, 5M)--Baker Ultrex grade or equivalent.
- Sodium acetate solution (NaOAc, 1.0M)--Dissolve 8.2 g NaOAc (Alfa Ultrapure grade or equivalent) in 100 mL water.
- Methyl isobutyl ketone (MIBK)--HPLC grade or equivalent.
- Phenol red indicator solution (0.04 percent w/v)--ACS reagent grade.

- Hydrochloric acid (HCl, 12M)--Baker Ultrex grade or equivalent.

- 2.5 M HCl--Dilute 208 mL of 12 M HCl to 1.0 L.

- $NH_4^+/NH_3$ buffer--Add 2.5M HCl to 21 mL of 5M $NH_4OH$ until the pH = 8.3, then dilute to 100 mL.

  NOTE: Do this cautiously in a fume hood.

- 8-hydroxyquinoline solution (10 g/L)--Dissolve 5 grams of 8-hydroxyquinoline (99 plus percent purity) in 12.5 mL HOAc, then dilute to 500 mL.

- 8-hydroxyquinoline sodium acetate reagent--Mix, in order, 10 mL 1.0M NaOAc, 50 mL water, and 10 mL hydroxyquinoline solution.

This reagent must be prepared daily.

### 12.11.4.2 Preparation of Aluminum Standard Solutions

- Aluminum stock solution--Prepare as described in section 12.11.3.1.

- Dilute calibration standards--Daily, quantitatively dilute the Al stock solution to prepare a series of calibration standards over the range 0 to 0.1 mg/L Al. A blank must be prepared. Prior to analysis, the blank, standards (and any QC samples) must be extracted.

  Step 1--Pipet 25.00 mL of a calibration standard (or calibration blank or QC sample) into a clean 50-mL separatory funnel (or a clean 50-mL disposable centrifuge tube with cap).

  Step 2--Add 2 to 3 drops phenol red indicator and 5.00 mL 8-hydroxyquinoline NaOAc reagent. Swirl to mix.

  Step 3--Rapidly adjust the pH to 8 by dropwise additions of 5M $NH_4OH$ until the solution turns red. Immediately add 2.0 mL $NH_4^+/NH_3$ buffer and 10 mL MIBK. Cap and shake vigorously for 7 to 10 seconds using a rapid, end-to-end motion. Be careful of pressure buildup.

  Step 4--Allow the phases to separate (10 to 15 seconds) and isolate the MIBK layer. If an emulsion forms, separation can be hastened by centrifugation. Keep the MIBK layer tightly capped to prevent evaporation.

### 12.11.4.3 Suggested Instrument Conditions (General)

- Drying cycle--Ramp 10 seconds, hold 10 seconds

- Drying temperature--100°C
- Ashing cycle--Ramp 5 seconds, hold 20 seconds
- Ashing temperature--1500°C
- Atomization cycle--Hold 5 seconds (no ramp, max. power heating)
- Atomization temperature--2500°C
- Purge gas--Argon at 20 cc/minute
- Lamp--Al HCl at 25 mA
- Wavelength--309.3 nm
- Graphite tube--Nonpyrolytic
- Sample size--25 µL

These operating conditions are for a Perkin-Elmer 5000 with a HGA-500 graphite furnace and AS-40 autosampler.

12.11.4.4 Analysis Procedure

Step 1--Calibrate the instrument as directed by the instrument manufacturer.

Step 2--Analyze the samples (including required QC samples).

Step 3--If a sample concentration exceeds the linear range, dilute with MIBK and reanalyze.

Report results as mg/L Al.

NOTE: By using the same volumes for standards as for samples, concentration factors are taken into account.

12.11.4.5 Precision and Accuracy--In a multiple lab study using 74 lake samples containing 0.005-3 mg/L extractable Al the overall duplicate relative standard deviation was 7.4 percent (note this is the overall within-lab precison).

Accuracy data are not available.

12.11.5 Procedure for Determination of Dissolved Calcium

Samples for determination of dissolved calcium (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for calcium (U.S. EPA, 1983).

12.11.5.1 Preparation of Reagents

- Lanthanum chloride matrix modifier solution ($LaCl_3$)--Dissolve 29 g $La_2O_3$, slowly and in small portions, in 250 mL concentrated HCl (Caution: Reaction is violent) and dilute to 500 mL with water.

12.11.5.2 Preparation of Calcium Standard Solutions

- Calcium stock solution (500 mg/L Ca)--Suspend 1.250 g $CaCO_3$ (analytical reagent grade, dried at 180°C for 1 hour before weighing) in water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 mL with water.

- Dilute calibration standards--Daily, quantitatively prepare a series of dilute Ca standards from the calcium stock solution to span the desired concentration range.

12.11.5.3 Suggested Instrumental Conditions (General)

- Lamp--Ca, hollow cathode

- Wavelength--422.7

  NOTE: The 239.9 nm line may also be used. This line has a relative sensitivity of 120.

- Fuel--acetylene

- Oxidant--air

- Flame--reducing

12.11.5.4 Analysis Procedure

Step 1--To each 10.0 mL volume of dilute calibration standard, blank, and sample add 1.00 mL $LaCl_3$ solution (e.g., add 2.0 mL $LaCl_3$ solution to 20.0 mL sample).

Step 2--Calibrate the instrument as directed by the manufacturer.

Step 3--Analyze the samples.

Step 4--Dilute and reanalyze any samples with a concentration exceeding the calibrated range.

Report results as mg/L Ca.

NOTE 1: Phosphate, sulfate and aluminum interfere but are masked by the addition of lanthanum. Because low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute acid solution. Concentrations of magnesium greater than 1,000 mg/L also cause low calcium values. Concentrations of up to 500 mg/L each of sodium, potassium, and nitrate cause no interference.

NOTE 2: Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.

NOTE 3: The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame.

12.11.5.5 Precision and Accuracy--In a single laboratory (EMSL-Cincinnati), using distilled water spiked at concentrations of 9.0 and 36 mg Ca/L, the standard deviations were ±0.3 and ±0.6, respectively. Recoveries at both these levels were 99 percent.

### 12.11.6 Procedure for Determination of Dissolved Iron

The samples for determination of dissolved ion (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy (U.S. EPA, 1983).

### 12.11.6.1 Preparation of Iron Standard Solutions

- Fe stock solution (1,000 mg/L Fe)--Carefully weigh 1.000 g pure iron wire (analytical reagent grade) and dissolve in 5 mL concentrated $HNO_3$, warming if necessary. When iron is completely dissolved, bring volume of solution to 1 L with water.

- Dilute calibration standards--Daily, quantitatively prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent (v/v) $HNO_3$).

### 12.11.6.2 Suggested Instrumental Conditions (General)

- Lamp--Fe, hollow cathode

- Wavelength--2.48.3 nm

NOTE: The following lines may also be used: 248.8 nm, relative sensitivity 2; 271.9 nm, relative sensitivity 4; 302.1 nm, relative sensitivity 5; 252.7 nm, relative sensitivity 6; 372.0 nm, relative sensitivity 10.

- Fuel--acetylene
- Oxidant--air
- Flame--oxidizing

12.11.6.3 Analysis Procedure

Step 1--Calibrate the instrument as directed by the instrument manufacturer.

Step 2--Analyze the samples.

Step 3--Dilute and reanalyze any samples with concentrations exceeding the calibrated range.

Report results in mg/L Fe.

12.11.6.4 Precision and Accuracy--An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL-Cincinnati. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead, and zinc were added to natural water samples. The statistical results for iron were as follows:

| Number Of Labs | True Value (μg/L) | Mean Value (μg/L) | Standard Deviation (μg/L) | Accuracy as % Bias |
|---|---|---|---|---|
| 82 | 840 | 855 | 173 | 1.8 |
| 85 | 700 | 680 | 178 | -2.8 |
| 78 | 350 | 348 | 131 | -0.5 |
| 79 | 438 | 435 | 183 | -0.7 |
| 57 | 24 | 58 | 69 | 141 |
| 54 | 10 | 48 | 69 | 382 |

12.11.7 Procedure for Determination of Dissolved Magnesium

The samples for determination of dissolved magnesium (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for magnesium.

12.11.7.1 Preparation of Reagents

- Lanthanum chloride solution ($LaCl_3$)--Dissolve 29 g $La_2O_3$, slowly and in small portions, in 250 mL concentrated HCl (Caution: Reaction is violent), and dilute to 500 mL with water.

12.11.7.2 Preparation of Magnesium Standard Solutions

- Stock solution (500 mg/L Mg)--Dissolve 0.829 g magnesium oxide, MgO (analytical reagent grade), in 10 mL of $HNO_3$ and dilute to 1 L with water.

- Dilute calibration standards--Daily, quantitatively prepare from the Mg stock solution a series of Mg standards that spans the desired concentration range.

12.11.7.3 Suggested Instrumental Conditions (General)

- Lamp--Mg, hollow cathode

- Wavelength--285.2 nm

  NOTE: The line at 202.5 nm may also be used. This line has a relative sensitivity of 25.

- Fuel--acetylene

- Oxidant--air

- Flame--oxidizing

12.11.7.4 Analysis Procedure

Step 1--To each 10.0 mL dilute calibration standard, blank, and sample, add 1.00 mL $LaCl_3$ solution (e.g., add 2.0 mL $LaCl_3$ solution to 20.0 mL sample).

Step 2--Calibrate the instrument as directed by the manufacturer.

Step 3--Analyze the samples.

Step 4--Dilute and reanalyze any samples with a concentration exceeding the linear range.

Report results as mg/L Mg.

NOTE 1: The interference caused by aluminum at concentrations greater than 2 mg/L is masked by addition of lanthanum. Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/L.

NOTE 2: To cover the range of magnesium values normally observed in surface waters (0.1 to 20 mg/L), it is suggested that either the 202.5 nm line be used or the burner head be rotated. A 90° rotation of the burner head will produce approximately one-eighth the normal sensitivity.

12.11.7.5 Precision and Accuracy--In a single laboratory (EMSL-Cincinnati), using distilled water spiked at concentrations of 2.1 and 8.2 mg/L Mg, the standard deviations were ±0.1 and ±0.2, respectively. Recoveries at both of these levels were 100 percent.

12.11.8 Procedure for Determination of Dissolved Manganese

The samples for determination of dissolved manganese (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for manganese (U.S. EPA, 1983).

12.11.8.1 Preparation of Manganese Standard Solutions

- Mn stock solution (1,000 mg/L Mn)--Carefully weigh 1.000 g manganese metal (analytical reagent grade) and dissolve in 10 mL of $HNO_3$. When metal is completely dissolved, dilute solution to 1 liter with 1 percent (v/v) HCl.
- Dilute calibration standards--Daily, quantitatively prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent (v/v) $HNO_3$).

12.11.8.2 Instrumental Conditions (General)

- Lamp--Mn, hollow cathode
- Wavelength--279.5 nm

  NOTE: The line at 403.1 nm may also be used. This line has a relative sensitivity of 10.

- Fuel--acetylene

- Oxidant--air

- Flame--oxidizing

12.11.8.3 Analysis Procedure

Step 1--Calibrate the instrument as directed by the manufacturer.

Step 2-- Analyze the samples.

Step 3--Dilute and reanalyze any samples with a concentration exeeding the calibrated range.

Report results as mg/L Mn.

12.11.8.4 Precision and Accuracy--An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL-Cincinnati. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead, and zinc were added to natural water samples. The statistical results for manganese were as follows:

| Number of Labs | True Value (μg/L) | Mean Value (μg/L) | Standard Deviation (μg/L) | Accuracy as % Bias |
|---|---|---|---|---|
| 77 | 426 | 432 | 70 | 1.5 |
| 78 | 469 | 474 | 97 | 1.2 |
| 71 | 84 | 86 | 26 | 2.1 |
| 70 | 106 | 104 | 31 | -2.1 |
| 55 | 11 | 21 | 27 | 93 |
| 55 | 17 | 21 | 20 | 22 |

12.11.9 Procedure for Determination of Dissolved Potassium

The samples for determination of dissolved potassium (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for potassium (U.S. EPA, 1983).

12.11.9.1 Preparation of Potassium Standard Solutions

- Potassium stock solution (100 mg/L K)--Dissolve 0.1907 g KCl (analytical reagent grade, dried at 110°C) in water and bring volume of solution to 1 L.

- Dilute calibration standards--Daily, quantitatively prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent (v/v) $HNO_3$).

12.11.9.2 Suggested Instrumental Conditions (General)

- Lamp--K, hollow cathode

- Wavelength--766.5 nm

  NOTE: The 404.4-nm line may also be used. This line has a relative sensitivity of 500.

- Fuel--acetylene

- Oxidant--air

- Flame--slightly oxidizing

12.11.9.3 Analysis Procedure

Step 1--Calibrate the instrument as directed by the manufacturer.

Step 2--Analyze the samples.

Step 3--Dilute and reanalyze any sample with a concentration exceeding the calibrated range.

Report results as mg/L K.

NOTE 1: In air-acetylene or other high-temperature flames (>2,800°C), potassium can experience partial ionization which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1,000 µg/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks should be analyzed to correct for potassium impurities in the buffer stock.

NOTE 2: To cover the range of potassium values normally observed in surface waters (0.1 to 20 mg/L), it is suggested that the burner head be rotated. A 90° rotation of the burner head provides approximately one-eighth the normal sensitivity.

12.11.9.4 Precision and Accuracy--In a single laboratory (EMSL-Cincinnati), using distilled water samples spiked at concentrations of 1.6 and 6.3 mg/L K, the standard deviations were ±0.2 and ±0.5, respectively. Recoveries at these levels were 103 percent and 102 percent, respectively.

### 12.11.10 Procedure for Determination of Dissolved Sodium

The samples for determination of dissolved sodium (filtered and preserved in the field) are analyzed by flame atomic absorption spectroscopy for sodium (U.S. EPA, 1983).

#### 12.11.10.1 Preparation of Sodium Standard Solutions

- Sodium stock solution (1,000 mg/L Na)--Dissolve 2.542 g NaCl (analytical reagent grade, dried at 140°C) in water and bring the volume of the solution to 1 L.
- Dilute calibration standards--Daily, quantitatively prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent (v/v) $HNO_3$).

#### 12.11.10.2 Suggested Instrumental Conditions (General)

- Lamp--Na, hollow cathode
- Wavelength--589.6 nm

  NOTE: The 330.2 nm resonance line of sodium, which has a relative sensitivity of 185, provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.

- Fuel--acetylene
- Oxidant--air
- Flame--oxidizing

#### 12.11.10.3 Analysis Procedure

Step 1--Calibrate the instrument as directed by the manufacturer.

Step 2--Analyze the samples.

Step 3--Dilute and reanalyze any samples with a concentration exceeding the calibrated range.

Report results as mg/L Na.

NOTE: Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1,000 mg/L) to both standards and samples.

12.11.10.4 Precision and Accuracy--In a single laboratory (EMSL-Cincinnati), using distilled water samples spiked at levels of 8.2 and 52 mg/L Na, the standard deviations were ±0.1 and ±0.8, respectively. Recoveries at these levels were 102 percent and 100 percent.

## 12.12 Calculations

Generally, instruments are calibrated to output sample results directly in concentration units. If they do not, then a manual calibration curve must be prepared and sample concentrations must be determined by comparing the sample signal to the calibrated curve. If dilutions were performed, the appropriate factor must be applied to sample values. Report results as mg/L for each analyte.

## 12.13 References

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## 13.0 DETERMINATION OF DISSOLVED METALS (Ca, Fe, Mg, and Mn) BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY

### 13.1 Scope and Application

This method is applicable to the determination of dissolved Ca, Fe, Mg, and Mn in natural surface waters.

Table 13.1 lists the recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization for the specified elements. Actual working detection limits are sample-dependent, and as the sample matrix varies, these concentrations may also vary.

Because of the differences among makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

### 13.2 Summary of Method

The method describes a technique for the simultaneous or sequential determination of Ca, Fe, Mg, and Mn in lake samples collected for the NSWS. The method is based on the measurement of atomic emission by optical spectroscopy. Samples are nebulized to produce an aerosol. The aerosol is transported by an argon carrier stream to an inductively coupled argon plasma (ICP), which is produced by a radio frequency (RF) generator. In the plasma (which is at a temperature of 6,000 to 10,000°K), the analytes in the aerosol are atomized, ionized, and excited. The excited ions and atoms emit light at their characteristic wavelengths. The spectra from all analytes are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed by a computer system. The signal is proportional to the analyte concentration and is calibrated by analyzing a series of standards (U.S. EPA, 1983; Fassel, 1982).

A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during sample analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and must reflect the same change in background intensity as occurs at the analyte wavelength measured. Generally, each instrument has different background handling capabilities. The instrument operating manual should be consulted for guidance.

TABLE 13.1. RECOMMENDED WAVELENGTHS[a] AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

| Element | Wavelength (nm) | Estimated detection limit (μg/L)[b] |
|---|---|---|
| Calcium | 317.933 | 10 |
| Iron | 259.940 | 7 |
| Magnesium | 279.079 | 30 |
| Manganese | 257.610 | 2 |

[a] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

[b] The estimated instrumental detection limits as shown are taken from Fassel, 1982. They are given as a guide for an instrumental limit. The actual method detection limits are sample-dependent and may vary as the sample matrix varies.

The possibility of additional interferences named in section 13.3 should also be recognized, and appropriate corrections should be made.

## 13.3 Interferences

Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They are summarized in sections 13.3.1 through 13.3.3.

### 13.3.1 Spectral Interferences

Spectral interferences can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from the line emission of high-concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 13.2 are some interference effects for the recommended wavelengths given in Table 13.1. The interference information is expressed as analyte concentration eqivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interfering element. The values in the table are only approximate and should be used as a guide for determining potential interferences. Actual values must be determined for each analytical system when necessary.

Only those interferences listed were investigated. The blank spaces in Table 13.2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 13.3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2 to 5 percent of the peaks generated by the analyte concentrations (also listed in Table 13.3).

### 13.3.2 Physical Interferences

Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples that contain high dissolved solids or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample or utilization of standard addition techniques.

High dissolved solids may also cause salt buildup at the tip of the nebulizer. This affects aerosol flow rate, causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem.

It has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

### 13.3.3 Chemical Interferences

Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are negligible with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (i.e., incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

TABLE 13.2. ANALYTE CONCENTRATION EQUIVALENTS (mg/L) ARISING FROM INTERFERENCES AT THE 100-mg/L LEVEL

| Analyte | Wavelength, (nm) | Interference | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Al | Ca | Cr | Cu | Fe | Mg | Mn | Ni | Ti | V |
| Calcium | 317.933 | -- | -- | 0.08 | -- | 0.01 | 0.01 | 0.04 | -- | 0.03 | 0.03 |
| Iron | 259.940 | -- | -- | -- | -- | -- | -- | 0.12 | -- | -- | -- |
| Magnesium | 279.079 | -- | 0.02 | 0.11 | -- | 0.13 | -- | 0.25 | -- | 0.07 | 0.12 |
| Manganese | 257.610 | 0.005 | -- | 0.01 | -- | 0.002 | 0.002 | -- | -- | -- | -- |

TABLE 13.3. INTERFERENCE AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR INTERFERENCE MEASUREMENTS IN TABLE 13.2

| Analytes | (mg/L) | Interferences | (mg/L) |
|---|---|---|---|
| Ca | 1 | Al | 1,000 |
| Fe | 1 | Ca | 1,000 |
| Mg | 1 | Cr | 200 |
| Mn | 1 | Cu | 200 |
| | | Fe | 1,000 |
| | | Mg | 1,000 |
| | | Nn | 200 |
| | | Ni | 200 |
| | | Ti | 200 |
| | | V | 200 |

### 13.3.4 Interference Tests

Whenever a new or unusual sample matrix is encountered, a series of tests should be performed prior to reporting concentration data for analyte elements. These tests, as outlined in sections 13.3.4.1 through 13.3.4.4, will ensure that neither positive nor negative interference effects are operative on any of the analyte elements, thereby distorting the accuracy of the reported values.

13.3.4.1 Serial Dilution--If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 percent of the original determination (or within some acceptable control limit that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

13.3.4.2 Spiked Addition--The recovery of a spiked addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect.

CAUTION: The standard addition technique does not detect coincident spectral overlap. If overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

13.3.4.3 Comparison with Alternate Method of Analysis--When investigating a new sample matrix, a comparison test may be performed with other analytical techniques, such as atomic absorption spectrometry or other approved methodology.

13.3.4.4 Wavelength Scanning of Analyte Line Region--If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

## 13.4 Safety

Generally, the calibration standards, sample types, and most reagents pose no hazard to the analyst. Protective clothing (lab coats and gloves) and safety glasses should be worn when handling concentrated acids.

Follow the instrument manufacturer's safety recommendations for the operation of the ICP.

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (NIOSH, 1977; OSHA, 1976; ACS, 1979) for the information of the analyst.

## 13.5 Apparatus and Equipment

- Inductively Coupled Plasma-Atomic Emission Spectrometer
- Computer-controlled ICP emission spectrometer with background correction capability.

## 13.6 Reagents and Consumable Materials

- Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent (e.g., Baker Ultrex grade or SeaStar Ultrapure grade).

  a. Hydrochloric Acid, concentrated (sp gr 1.19)

  b. Hydrochloric Acid (50 percent v/v)--Add 500 mL concentrated HCl to 400 mL water and dilute to 1 L.

  c. Nitric Acid, concentrated (sp gr 1.41)

d. Nitric Acid (50 percent v/v)--Add 500 mL concentrated $HNO_3$ to 400 mL water and dilute to 1 L.

- Water--Water must meet the specifications for Type I Reagent Water given in ASTM D 1193 (ASTM, 1984).

- Standard Stock Solutions--Solutions may be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for 1 hour at 105°C unless otherwise specified.

CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

a. Calcium Stock Standard Solution (100 mg/L)--Suspend 0.2498 g $CaCO_3$ (dried at 180°C for 1 hour before weighing) in water and dissolve cautiously with a minimum amount of 50 percent $HNO_3$. Add 10.0 mL concentrated $HNO_3$ and dilute to 1,000 mL with water.

b. Iron Stock Standard Solution (100 mg/L)--Dissolve 0.1430 g $Fe_2O_3$ in a warm mixture of 20 mL 50 percent HCl and 2 mL concentrated $HNO_3$. Cool, add an additional 5 mL concentrated $HNO_3$, and dilute to 1,000 mL with water.

c. Magnesium Stock Standard Solution (100 mg/L)--Dissolve 0.1658 g MgO in a minimum amount of 50 percent $HNO_3$. Add 10.0 mL concentrated $HNO_3$ and dilute to 1,000 mL with water.

d. Manganese Stock Standard Solution (100 mg/L)--Dissolve 0.1000 g of manganese metal in an acid mixture consisting of 10 mL concentrated HCl and 1 mL concentrated $HNO_3$, and dilute to 1,000 mL with water.

## 13.7 Sample Handling, Preservation, and Storage

For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Labware should be thoroughly washed as described in Appendix A.

Samples are collected and processed in the field. A portion (aliquot 3) of each sample is filtered and acidified (0.1-mL increments) with nitric acid until the pH <2. The processed samples are then sent to the lab and are analyzed (as is) for dissolved metal (Ca, Fe, Ma, Mn) content.

## 13.8 Calibration and Standardization

Prepare a calibration blank and a series of dilute calibration standards from the stock solutions spanning the expected sample concentration range. Match the acid content of the standards to that of the samples (written on the sample label, ca. 0.2 percent). A multi-element standard may be prepared.

The calibration procedure varies with the various ICPES instruments. Calibrate the ICPES for each analyte following the instrument operating conditions.

## 13.9 Quality Control

The required QC procedures are described in Section 3.4.

## 13.10 Procedure

Step 1--Set up instrument as recommended by the manufacturer or as experience dictates. The instrument must be allowed to become thermally stable before beginning (10 to 30 minutes).

Step 2--Profile and calibrate instrument according to instrument manufacturer's recommended procedures. Flush the system with the calibration blank between each standard. (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

Step 3--Begin sample analysis, flushing the system with the calibration blank solution between each sample. Remember to analyze required QC samples.

Step 4--Dilute and reanalyze any samples with a concentration exceeding the calibration range.

## 13.11 Calculations

Generally, instruments are calibrated to output sample results directly in concentration units. If not, then a manual calibration curve must be prepared and sample concentrations determined by comparing the sample signal to the calibrated curve. If dilutions were performed, the appropriate factor must be applied to sample values. Report results as mg/L for each analyte.

## 13.12 Precision and Accuracy

In an EPA round-robin phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 13.4 lists the true value, the mean reported value, and the mean %RSD (U.S. EPA, 1983).

## 13.13 References

American Chemical Society, 1979. Safety in Academic Laboratories, 3rd ed. Committee on Chemical Safety, ACS, Washington, D.C.

American Society for Testing and Materials, 1984. Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water, D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Department of Health, Education, and Welfare, 1977. Carcinogens - Working with Carcinogens. No. 77-206. DHEW, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, Ohio.

Fassel, V. A., 1982. Analytical Spectroscopy with Inductively Coupled Plasmas - Present Status and Future Prospects. In: Recent Advances in Analytical Spectroscopy. Pergamon Press, Oxford and New York.

Occupational Safety and Health Administration, 1976. OSHA Safety and Health Standards, General Industry. OSHA 2206 (29 CFR 1910). OSHA.

U.S. Environmental Protection Agency, 1979. Inductively Coupled Plasma - Atomic Emission Spectroscopy - Prominent Lines. EPA-600/4-79-017. U.S. EPA, Cincinnati, Ohio.

U.S. Environmental Protection Agency, 1983 (revised). Methods for Chemical Analysis of Water and Wastes, Method 200.7, Inductively Coupled Plasma-Atomic Emission Spectrometric Method for the Trace Element Analysis of Water and Wastes. EPA-600/4-79-020. U.S. EPA, Cincinnati, Ohio.

TABLE 13.4. ICP PRECISION AND ACCURACY DATA[1]

| Element | Sample 1<br>True Value (µg/L) | Sample 1<br>Mean Reported Value (µg/L) | Sample 1<br>Mean %RSD | Sample 2<br>True Value (µg/L) | Sample 2<br>Mean Reported Value (µg/L) | Sample 2<br>Mean %RSD | Sample 3<br>True Value (µg/L) | Sample 3<br>Mean Reported Value (µg/L) | Sample 3<br>Mean %RSD |
|---|---|---|---|---|---|---|---|---|---|
| Mn | 350 | 345 | 2.7 | 15 | 15 | 6.7 | 100 | 99 | 3.3 |
| Fe | 600 | 594 | 3.0 | 20 | 19 | 15 | 180 | 178 | 6.0 |

[1] Not all elements were analyzed by all laboratories.
Ca and Mg were not determined.

# APPENDIX A

## CLEANING OF PLASTICWARE

A laboratory supplies clean plastic sample containers (cubitainers, Nalgene bottles, centrifuge tubes) to the field stations. The containers are composed of amber, high-density linear polyethylene, and are of the wide-mouth design. Each lake sample requires one 4-L cubitainer, one 500-mL capacity bottle, two 250-mL capacity bottles, three 125-mL capacity bottles, one 50-mL graduated centrifuge tube with cap, and one 10-mL centrifuge tube with cap. Samples that are split require additional containers, as indicated in Table 2.4. The equipment list, Table 2.1, contains names of suitable brands of each container.

Plasticware, depending on its use, is cleaned by either an acid leaching procedure or water leaching procedure:

### Cleaning Procedure 1 (Acid Leaching)

All plasticware (with the exceptions in the next paragraph) is rinsed three times with deionized water, three times with 3N $HNO_3$ (prepared from Baker Instra-Analyzed $HNO_3$ or equivalent), and six times with deionized water. It is then filled with deionized water and allowed to stand for 48 hours. Next, it is emptied, dried in a laminar-flow hood delivering Class 100 air (when dry containers are necessary), and placed in clean plastic bags (bottles are capped first).

### Cleaning Procedure 2 (DI Water Leaching)

Plasticware to be used for pH, acidity, alkalinity, and anion determinations is rinsed three times with deionized water, filled with deionized water, allowed to stand for 48 hours, then emptied and sealed in clean plastic bags.

NOTE: The deionized water used in cleaning the plasticware must meet or exceed specifications for ASTM Type I reagent grade water.

After the initial cleaning (by procedure 1 or procedure 2), 5 percent of the containers are checked to ensure that rinsing has been adequate. The check is made by first adding 500 mL (or maximum amount) deionized water to a clean container, sealing the container with a cap or parafilm, and slowly rotating it so that the water touches all surfaces. The specific conductance of the water is then measured. It must be less than 1 µS/cm. If any of the containers fail the check, all of the containers are rerinsed and 5 percent are retested.

# APPENDIX B

## BLANK DATA FORMS

The National Surface Water Survey forms shown in this appendix are facsimiles of the forms used in the laboratory.

NATIONAL SURFACE WATER SURVEY
FORM 11

SUMMARY OF SAMPLE RESULTS

LAB NAME ____________________ BATCH ID __________ LAB MANAGER'S SIGNATURE ______________________________

| | ALIQUOT ID | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | | | | | | 2 | 3 | | | | |
| SAMPLE ID: | Ca mg/L | Mg mg/L | K mg/L | Na mg/L | Mn mg/L | Fe mg/L | Extr. Al mg/L | Cl mg/L | $SO_4^{2-}$ mg/L | $NO_3^-$ mg/L | $SiO_2$ mg/L | ISE Total $F^-$ mg/L |
| 01 | | | | | | | | | | | | |
| 02 | | | | | | | | | | | | |
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NOTE: Approved Data Qualifiers and instructions for their use are listed in Table 3.10.

NSWS Form 11

# NATIONAL SURFACE WATER SURVEY
FORM 11

## SUMMARY OF SAMPLE RESULTS

LAB NAME ________________ BATCH ID __________ LAB MANAGER'S SIGNATURE ________________

| SAM-PLE ID: | ALIQUOT ID | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 4 | | 5 | | | | | | | | 6 | 7 |
| | | | Measured | | | | | | | | | |
| | DOC mg/L | $NH_4^+$ mg/L | Eq. pH | Alk Init. pH | Acy Init. pH | Acy µeq/L | Alk µeq/L | COND. µS/cm | Eq. DIC mg/L | Init. DIC mg/L | Total P mg/L | Total Al mg/L |
| 01 | | | | | | | | | | | | |
| 02 | | | | | | | | | | | | |
| 03 | | | | | | | | | | | | |
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NOTE: Approved Data Qualifiers and instructions for their use are listed in Table 3.10.

NSWS Form 11 (Continued)

## NATIONAL SURFACE WATER SURVEY
Form 13

## ALKALINITY AND ACIDITY RESULTS

Lab Name ____________ Batch ID ____________ Sample ID ____________
Lab Manager's Signature ____________ Analyst ____________

**RESULTS**

[Alk] = ____________ µeq/L

**DATA**

$C_A$ = ____________ eq/L DATE STANDARDIZED ____________
$C_B$ = ____________ eq/L DATE STANDARDIZED ____________

INITIAL SAMPLE VOLUME ____________ mL
BLANK ALKALINITY ____________

ACID TITRATION

| VOLUME HCl (mL) | MEASURED pH' | CALCULATED pH |
|---|---|---|
| 0.00 | | |
| 0.00 (with KCl) | | |
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BASE TITRATION

| VOLUME NaOH (mL) | MEASURED pH' | CALCULATED pH |
|---|---|---|
| 0.00 | | |
| 0.00 (with KCl) | | |
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### NATIONAL SURFACE WATER SURVEY
Form 14*

### QC DATA FOR ALKALINITY AND ACIDITY ANALYSES

LAB NAME ______________________ BATCH ID ____________

LAB MANAGER'S SIGNATURE ______________________________

| SAMPLE ID | Alk µeq/L | $CO_2$-Acy µeq/L | CALCULATED Alk | | %X[b] |
|---|---|---|---|---|---|
| | | | RESULT | DIFFERENCE[a] | |
| 01 | | | | | |
| 02 | | | | | |
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| 04 | | | | | |
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*Form not required in data package but recommended for internal QC requirements.

[a] Difference = Calculated Alk-Measured Alk

[b] $$\%X = \frac{\text{DIC (in } \mu\text{moles/L)} - ([\text{Alk}] + [CO_2\text{-Acy}])}{\text{DIC}} \times 100$$

NSWS Form 14*

# NATIONAL SURFACE WATER SURVEY
Form 15*

## CONDUCTIVITY

LAB NAME ____________________ BATCH ID ______________

LAB MANAGER'S SIGNATURE __________________

| Sample ID | SPECIFIC CONDUCTANCE (µS/cm) |  |  | CALCULATED CONDUCTANCE FOR EACH ION µS/cm |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Calculated | Measured | %D** | $HCO_3^-$ | $Ca^{+2}$ | $CO_3^{-2}$ | $Cl^-$ | $Mg^{+2}$ | $NO_3^-$ | $K^+$ | $Na^+$ | $SO_4^{-2}$ | $NH_4^+$ | $H^+$ | $OH^-$ |
| 01 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 02 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 03 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
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| 30 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Specific Conductance Factors of Ions [(µS/cm at 25°C) per mg/L] |  |  |  | 0.715 | 2.60 | 2.82 | 2.14 | 3.82 | 1.15 | 1.84 | 2.13 | 1.54 | 4.13 | $3.5 \times 10^5$ (per mole/L) | $1.92 \times 10^5$ (per mole/L) |

* Form not required in data package but recommended for internal QC requirements

$$\text{** \% Conductance Difference} = \frac{\text{Calculated Cond.} - \text{Measured Cond.}}{\text{Measured Conductance}} \times 100$$

NSWS Form 15

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## NATIONAL SURFACE WATER SURVEY
Form 16*

## ANION-CATION BALANCE CALCULATION

LAB NAME ____________________ BATCH ID ________ LAB MANAGERS SIGNATURE ______________

| Sample ID | % Ion Difference ** | Ions - (µeq/L) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $Ca^{+2}$ | $Cl^-$ | $Mg^{+2}$ | $NO_3^-$ | $K^+$ | $Na^+$ | $SO_4^{-2}$ | $F^-$ | $NH_4^+$ | ALK | $H^+$*** |
| 01 | | | | | | | | | | | | |
| 02 | | | | | | | | | | | | |
| 03 | | | | | | | | | | | | |
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| 23 | | | | | | | | | | | | |
| 24 | | | | | | | | | | | | |
| 25 | | | | | | | | | | | | |
| 26 | | | | | | | | | | | | |
| 27 | | | | | | | | | | | | |
| 28 | | | | | | | | | | | | |
| 29 | | | | | | | | | | | | |
| 30 | | | | | | | | | | | | |
| Factor to Convert mg/L to µeq/L | | 49.9 | 28.2 | 82.3 | 16.1 | 25.6 | 43.5 | 20.8 | 52.6 | 55.4 | ---- | ---- |

* Form not required in data package but recommended for internal QC requirements

$$\text{** \% Ion Difference} = \frac{\text{Alk} + \Sigma\ \text{Anions} - \Sigma\ \text{Cations (except } H^+)}{\Sigma\ \text{Anions} + \Sigma\ \text{Cation} + \text{Alk} + 2[H^+]} \times 100$$

$$\text{***}\ [H^+] = (10^{-pH}) \times 10^6$$

NATIONAL SURFACE WATER SURVEY
Form 17

Page 1 of 1

# IC RESOLUTION TEST

LAB NAME ______________________________

BATCH ID ______________________________

LAB MANAGER'S SIGNATURE ___________________________

---

IC Resolution Test

IC Make and Model: ___________________________

Date: __________________

Concentration: $SO_4^{2-}$ __________________ µg/mL, $NO_3^-$ ____________ µg/mL

Column Back Pressure (at max. of stroke): ____________________ psi

Flow Rate: ________________ mL/min

Column Model: _______________________ Date of Purchase: ____________________

Column Manufacturer: ________________________________

Column Serial No: __________________________________

Is precolumn in system ____ Yes ____ No

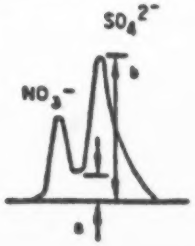
(a) __________ cm (b) __________ cm

Percentage Resolution: 100 x (1-a/b) ________________________

The resolution must be greater than 60%

---

Test Chromatogram:



NSWS Form 17

## NATIONAL SURFACE WATER SURVEY
Form 18

## QUALITY ASSURANCE
(DETECTION LIMITS)

LAB NAME ______________________ BATCH ID ________________

LAB MANAGER'S SIGNATURE ______________________________

| Parameter | Units | Contract Required Detection Limit | Instrumental Detection Limit | Date Determined (DD MMM YY) |
|---|---|---|---|---|
| Ca | mg/L | 0.01 | | |
| Mg | mg/L | 0.01 | | |
| K | mg/L | 0.01 | | |
| Na | mg/L | 0.01 | | |
| Mn | mg/L | 0.01 | | |
| Fe | mg/L | 0.01 | | |
| Total Extractable Al | mg/L | 0.005 | | |
| $Cl^-$ | mg/L | 0.01 | | |
| $SO_4^{2-}$ | mg/L | 0.05 | | |
| $NO_3^-$ | mg/L | 0.005 | | |
| $SiO_2$ | mg/L | 0.05 | | |
| Total $F^-$ | mg/L | 0.005 | | |
| $NH_4^+$ | mg/L | 0.01 | | |
| DOC | mg/L | 0.1 | | |
| Specific Conductance | µS/cm | * | | |
| DIC | mg/L | 0.05 | | |
| Total P | mg/L | 0.002 | | |
| Total Al | mg/L | 0.005 | | |

*Report the $\overline{X}$, which must not exceed 0.9 µS/cm, of six (6) nonconsecutive blanks.

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# NATIONAL SURFACE WATER SURVEY
FORM 19

## SAMPLE HOLDING TIME SUMMARY

LAB NAME ____________ BATCH ID ________ LAB MANAGER'S SIGNATURE ____________________

DATE* SAMPLED ____________ DATE RECEIVED ______

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | Ca | Mg | K | Na | Mn | Fe | Total Extr. Al | Cl | SO | NO | $SiO_2$ | ISE Total $F^-$ |
| Holding Time | 28 | 28 | 28 | 28 | 28 | 28 | 7 | 28 | 28 | 7 | 28 | 28 |
| Holding Time Plus Date Sampled | | | | | | | | | | | | |
| Sample ID: | | | | Date* | | | | Analyzed** | | | | |
| 01 | | | | | | | | | | | | |
| 02 | | | | | | | | | | | | |
| 03 | | | | | | | | | | | | |
| 04 | | | | | | | | | | | | |
| 05 | | | | | | | | | | | | |
| 06 | | | | | | | | | | | | |
| 07 | | | | | | | | | | | | |
| 08 | | | | | | | | | | | | |
| 09 | | | | | | | | | | | | |
| 10 | | | | | | | | | | | | |
| 11 | | | | | | | | | | | | |
| 12 | | | | | | | | | | | | |
| 13 | | | | | | | | | | | | |
| 14 | | | | | | | | | | | | |
| 15 | | | | | | | | | | | | |
| 16 | | | | | | | | | | | | |
| 17 | | | | | | | | | | | | |
| 18 | | | | | | | | | | | | |
| 19 | | | | | | | | | | | | |
| 20 | | | | | | | | | | | | |
| 21 | | | | | | | | | | | | |
| 22 | | | | | | | | | | | | |
| 23 | | | | | | | | | | | | |
| 24 | | | | | | | | | | | | |
| 25 | | | | | | | | | | | | |
| 26 | | | | | | | | | | | | |
| 27 | | | | | | | | | | | | |
| 28 | | | | | | | | | | | | |
| 29 | | | | | | | | | | | | |
| 30 | | | | | | | | | | | | |

*Report these dates as Julian dates (i.e., March 26, 1984 = 4086).

**If parameter was reanalyzed due to QA problems, report the last date analyzed.

# NATIONAL SURFACE WATER SURVEY
FORM 19

## SAMPLE HOLDING TIME SUMMARY

LAB NAME ____________________ BATCH ID __________ LAB MANAGER'S SIGNATURE ______________________

DATE* SAMPLED ________________ DATE RECEIVED ______

| Parameter | DOC | $NH_4^+$ | Eq. pH | Acidity | Alkalinity | Specific Conductance | Eq. DIC | Init. DIC | Total P | Total Al |
|---|---|---|---|---|---|---|---|---|---|---|
| Holding Time | 14 | 28 | 7 | 14 | 14 | 14 | 14 | 14 | 28 | 28 |
| Holding Time Plus Date Sampled | | | | | | | | | | |
| Sample ID: | | | Date* | | | Analyzed** | | | | |
| 01 | | | | | | | | | | |
| 02 | | | | | | | | | | |
| 03 | | | | | | | | | | |
| 04 | | | | | | | | | | |
| 05 | | | | | | | | | | |
| 06 | | | | | | | | | | |
| 07 | | | | | | | | | | |
| 08 | | | | | | | | | | |
| 09 | | | | | | | | | | |
| 10 | | | | | | | | | | |
| 11 | | | | | | | | | | |
| 12 | | | | | | | | | | |
| 13 | | | | | | | | | | |
| 14 | | | | | | | | | | |
| 15 | | | | | | | | | | |
| 16 | | | | | | | | | | |
| 17 | | | | | | | | | | |
| 18 | | | | | | | | | | |
| 19 | | | | | | | | | | |
| 20 | | | | | | | | | | |
| 21 | | | | | | | | | | |
| 22 | | | | | | | | | | |
| 23 | | | | | | | | | | |
| 24 | | | | | | | | | | |
| 25 | | | | | | | | | | |
| 26 | | | | | | | | | | |
| 27 | | | | | | | | | | |
| 28 | | | | | | | | | | |
| 29 | | | | | | | | | | |
| 30 | | | | | | | | | | |

*Report these dates as Julian dates (i.e., March 26, 1984 = 4086).
**If parameter was reanalyzed due to QA problems, report the last date analyzed.

NSWS Form 19 (Continued)

# NATIONAL SURFACE WATER SURVEY
## FORM 20

## BLANKS AND QCCS

LAB NAME ____________ BATCH ID ____________ LAB MANAGER'S SIGNATURE ____________

|  | ALIQUOT ID |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | 1 |  |  |  |  |  | 2 | 3 |  |  |  |  |
| Parameter | Ca mg/L | Mg mg/L | K mg/L | Na mg/L | Mn mg/L | Fe mg/L | Total Extr.Al mg/L | $Cl^-$ mg/L | $SO_4^{2-}$ mg/L | $NO_3^-$ mg/L | $SiO_2$ mg/L | ISE Total $F^-$ mg/L |
| Calibration Blank |  |  |  |  |  | N | N | N<br>N | N<br>N | N<br>N | N | N<br>N |
| Reagent Blank | N | N | N | N | N |  |  | N | N | N | N | N |
| DL QCCS Theoretical |  |  |  |  |  |  |  |  |  |  |  |  |
| DL QCCS Measured |  |  |  |  |  |  |  |  |  |  |  |  |
| Low QCCS True Value |  |  |  |  |  |  |  |  |  |  |  |  |
| Low QCCS Upper Control Limit |  |  |  |  |  |  |  |  |  |  |  |  |
| Low QCCS Lower Control Limit |  |  |  |  |  |  |  |  |  |  |  |  |
| Initial |  |  |  |  |  |  |  |  |  |  |  |  |
| Continuing |  |  |  |  |  |  |  |  |  |  |  |  |
| Continuing |  |  |  |  |  |  |  |  |  |  |  |  |
| Continuing |  |  |  |  |  |  |  |  |  |  |  |  |
| Continuing |  |  |  |  |  |  |  |  |  |  |  |  |
| Continuing |  |  |  |  |  |  |  |  |  |  |  |  |
| Final |  |  |  |  |  |  |  |  |  |  |  |  |
| High QCCS True Value |  |  |  |  |  |  |  |  |  |  |  |  |
| High QCCS Upper Control Unit |  |  |  |  |  |  |  |  |  |  |  |  |
| High QCCS Lower Control Limit |  |  |  |  |  |  |  |  |  |  |  |  |
| Initial |  |  |  |  |  |  |  |  |  |  |  |  |
| Continuing |  |  |  |  |  |  |  |  |  |  |  |  |
| Final |  |  |  |  |  |  |  |  |  |  |  |  |

Note: Approved Data Qualifiers and instruction for their use are listed in Table 3.10.

NSWS Form 20

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## NATIONAL SURFACE WATER SURVEY
## FORM 20

## BLANKS AND QCCS

LAB NAME __________ BATCH ID __________ LAB MANAGER'S SIGNATURE __________

| | ALIQUOT ID | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 4 | | 5 | | | | | | 6 | 7 |
| | | | Measured | | | | | | | |
| Parameter | DOC mg/L | $NH_4^+$ mg/L | Eq pH | Alk pH | Acy pH | Cond. µS/cm | Eq. DIC mg/L | Init. DIC mg/L | Total P mg/L | Total Al mg/L |
| Calibration Blank | | | N | N | N | | | | | |
| Reagent Blank | N | N | N | N | N | N | N | N | N | |
| DL theoretical | N | N | N | N | N | N | N | N | | |
| QCCS measured | N | N | N | N | N | N | N | N | | |
| Low QCCS True Value | | | | | | | | | | |
| Low QCCS Upper Control Limit | | | | | | | | | | |
| Low QCCS Lower Control Limit | | | | | | | | | | |
| Initial | | | | | | | | | | |
| Continuing | | | | | | | | | | |
| Continuing | | | | | | | | | | |
| Continuing | | | | | | | | | | |
| Continuing | | | | | | | | | | |
| Continuing | | | | | | | | | | |
| Final | | | | | | | | | | |
| High QCCS True Value | | | | | | | | | | |
| High QCCS Upper Control Limit | | | | | | | | | | |
| High QCCS Lower Control Limit | | | | | | | | | | |
| Initial | | | | | | | | | | |
| Continuing | | | | | | | | | | |
| Final | | | | | | | | | | |

Note: Approved Data Qualifiers and instruction for their use are listed in Table 3.10

NSWS Form 20 (Continued)

### NATIONAL SURFACE WATER SURVEY
### FORM 21

### MATRIX SPIKES

| | ALIQUOT ID | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | | | | | | 3 | | | | | 4 | | 6 | 7 |
| Parameter | Ca mg/L | Mg mg/L | K mg/L | Na mg/L | Mn mg/L | Fe mg/L | Cl mg/L | $SO_4^{2-}$ mg/L | $NO_3^-$ mg/L | $SiO_2$ mg/L | ISE Total F mg/L | DOC mg/L | $NH_4^+$ mg/L | Total P mg/L | Total Al mg/L |
| MS First (orig.) Sample ID | | | | | | | | | | | | | | | |
| Sample Result | | | | | | | | | | | | | | | |
| Spike Result | | | | | | | | | | | | | | | |
| Spike Added | | | | | | | | | | | | | | | |
| Percent Recovery | | | | | | | | | | | | | | | |
| MS Second Sample ID | | | | | | | | | | | | | | | |
| Sample Result | | | | | | | | | | | | | | | |
| Spike Result | | | | | | | | | | | | | | | |
| Spike Added | | | | | | | | | | | | | | | |
| Percent Recovery | | | | | | | | | | | | | | | |
| MS Third Sample ID | | | | | | | | | | | | | | | |
| Sample Result | | | | | | | | | | | | | | | |
| Spike Result | | | | | | | | | | | | | | | |
| Spike Added | | | | | | | | | | | | | | | |
| Percent Recovery | | | | | | | | | | | | | | | |

Note: Matrix spikes not required for aliquots 2 and 5.

NSWS Form 21

# NATIONAL SUFACE WATER SURVEY
Form 22

## DUPLICATES

LAB NAME ______________ BATCH ID ________ LAB MANAGER'S SIGNATURE ______________

| | ALIQUOT ID | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | | | | | | 2 | 3 | | | | |
| Parameter | Ca mg/L | Mg mg/L | K mg/L | Na mg/L | Mn mg/L | Fe mg/L | Total Extr.Al mg/L | $Cl^-$ mg/L | $SO_4^{2-}$ mg/L | $NO_3$ mg/L | $SiO_2$ mg/L | ISE Total $F^-$ mg/L |
| Duplicate Sample ID | | | | | | | | | | | | |
| Sample Result | | | | | | | | | | | | |
| Duplicate Result | | | | | | | | | | | | |
| % RSD | | | | | | | | | | | | |
| Second Duplicate Sample ID | | | | | | | | | | | | |
| Sample Result | | | | | | | | | | | | |
| Duplicate Result | | | | | | | | | | | | |
| % RSD | | | | | | | | | | | | |
| Third Duplicate Sample ID | | | | | | | | | | | | |
| Sample Result | | | | | | | | | | | | |
| Duplicate Result | | | | | | | | | | | | |
| % RSD | | | | | | | | | | | | |

Note: Approved Data Qualifiers and instructions for their use are listed in Table 3.10.

## NATIONAL SURFACE WATER SURVEY
Form 22

Page 2 of 2

## DUPLICATES

LAB NAME ____________ BATCH ID ________ LAB MANAGER'S SIGNATURE ______

| Parameter | ALIQUOT ID | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 4 | | 5 | | | | | | | | 6 | 7 |
| | | | Measured | | | | | | | | | |
| | DOC mg/L | $NH_4^+$ mg/L | Eq. pH | Alk Initial pH | Acy Initial pH | $CO_2$-Acy µeq/L | Alk µeq/L | Cond. µS/cm | Eq. DIC mg/L | Init. DIC mg/L | Total P mg/L | Total Al mg/L |
| Duplicate Sample ID | | | | | | | | | | | | |
| Sample Result | | | | | | | | | | | | |
| Duplicate Result | | | | | | | | | | | | |
| % RSD* | | | | | | | | | | | | |
| Second Duplicate Sample ID | | | | | | | | | | | | |
| Sample Result | | | | | | | | | | | | |
| Duplicate Result | | | | | | | | | | | | |
| % RSD* | | | | | | | | | | | | |
| Third Duplicate Sample ID | | | | | | | | | | | | |
| Sample Result | | | | | | | | | | | | |
| Duplicate Result | | | | | | | | | | | | |
| % RSD* | | | | | | | | | | | | |

Note: Approved Data Qualifiers and instructions for their use are listed in 3.10.
*Report absolute difference rather than RSD for pH determinations.

NSWS Form 22 (Continued)

NATIONAL SURFACE WATER SURVEY
Form 23

STANDARD ADDITIONS

| Parameter | ALIQUOT ID 1 | | | | | | 3 | | | | | 4 | | 6 | 7 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ca mg/L | Mg mg/L | K mg/L | Na mg/L | Mn mg/L | Fe mg/L | Cl mg/L | $SO_4^{2-}$ mg/L | $NO_3^-$ mg/L | $SiO_2$ mg/L | ISE Total F- mg/L | DOC mg/L | $NH_4^+$ mg/L | Total P mg/L | Total Al mg/L |
| MS First (orig.) Sample ID | | | | | | | | | | | | | | | |
| Single Response | | | | | | | | | | | | | | | |
| Spike added (Conc.) | | | | | | | | | | | | | | | |
| Sample Spike 1 Response | | | | | | | | | | | | | | | |
| Spike 2 Conc. | | | | | | | | | | | | | | | |
| Sample Spike 2 Response | | | | | | | | | | | | | | | |
| Calc. Sample Conc. for Orig. Sample (Summarized on Form 11) | | | | | | | | | | | | | | | |

Note: Approved Data Qualifiers and instructions for their use are lested in Table 3.10.

# APPENDIX C

# EXAMPLES OF CALCULATIONS REQUIRED FOR ALKALINITY AND ACIDITY DETERMINATIONS

## 1.0 HCl STANDARDIZATION (TEXT SECTION 4.8.1)

1.00 mL of a 0.01038N $Na_2CO_3$ plus 40.00 mL $CO_2$-free deionized water is titrated with HCl titrant. The titration data are given below.

| mL HCl added | pH | mL HCl added | pH | mL HCl added | pH |
|---|---|---|---|---|---|
| 0.00 | 10.23 | 0.800 | 6.37 | 1.700 | 3.84 |
| 0.100 | 9.83 | 0.900 | 6.03 | 1.900 | 3.72 |
| 0.200 | 9.70 | 1.000 | 5.59 | 2.100 | 3.63 |
| 0.300 | 9.54 | 1.100 | 4.91 | 2.300 | 3.56 |
| 0.400 | 9.28 | 1.200 | 4.48 | 2.500 | 3.49 |
| 0.500 | 8.65 | 1.300 | 4.26 | | |
| 0.600 | 7.20 | 1.400 | 4.11 | | |
| 0.700 | 6.71 | 1.500 | 4.00 | | |

$F_{1b}$ is calculated for the data sets (V, pH) with pH 4-7 using the equation

$$F_{1b} = (V_s + V)\left[\frac{V_s C}{(V_s + V)}\left(\frac{[H^+]K_1 + 2\,K_1\,K_2}{[H^+]^2 + [H^+]K_1 + K_1\,K_2}\right) + \frac{K_w}{[H^+]} - [H^+]\right]$$

where

$V_s$ = initial sample volume = 41.0 mL
$V$ = volume of HCl added.
$C$ = $1.266 \times 10^{-4}$ = $(N\ Na_2CO_3)/(2 \times 41)$
$[H^+]$ = $10^{-pH}$
$K_1$ = $4.3 \times 10^{-7}$
$K_2$ = $5.61 \times 10^{-11}$
$K_w$ = $1.01 \times 10^{-14}$

The ($V$, $F_{1b}$) values are tabulated below.

| $V$ | $F_{1b}$ ($\times 10^{-3}$) | $V$ | $F_{1b}$ ($\times 10^{-3}$) |
|---|---|---|---|
| 0.700 | 3.57 | 1.100 | -0.34 |
| 0.800 | 2.59 | 1.200 | -1.33 |
| 0.900 | 1.60 | 1.300 | -2.28 |
| 1.000 | 0.64 | 1.400 | -3.26 |
|  |  | 1.500 | -4.23 |

The plot of $F_{1b}$ versus $V$ is shown in Figure C-1. The data lie on a straight line and are analyzed by linear regression to obtain the coefficients of the line

$$F_{1b} = a + bV$$

from the regression,

$r = 1.0000$
$a = 0.01038 \pm 0.00001$
$b = -0.009747 \pm 0.000012$

Then $V_1 = -a/b = 1.065$ mL

and

$$N_{HCl} = \frac{N\ Na_2CO_3 \times V\ Na_2CO_3}{V_1} = \frac{(0.01038)\ (1.00)}{1.065} = 0.009743 \text{ eq/L}$$

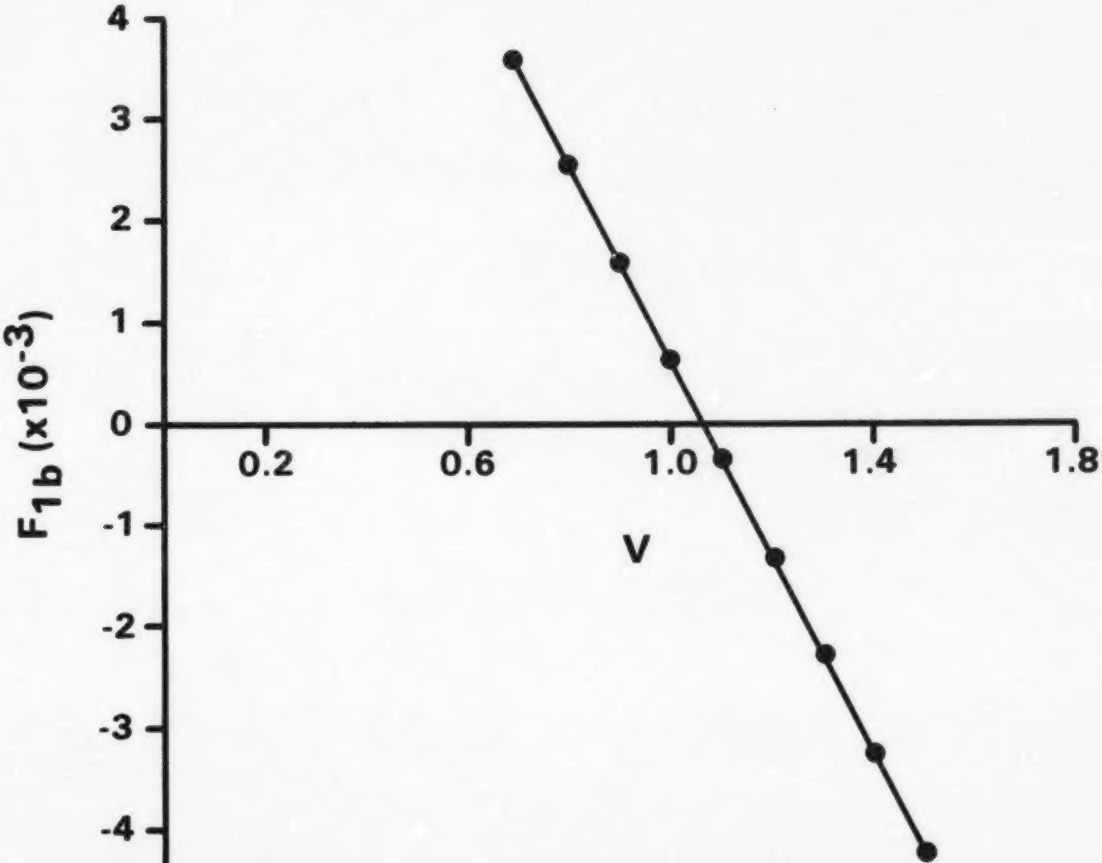

Figure C-1. Plot of $F_{1b}$ versus V for HCl standardization.

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## 2.0 NaOH STANDARDIZATION (TEXT SECTION 4.8.2)

### 2.1 Initial NaOH Standardization with KHP (Text Section 4.8.2.1)

5.00 mL of $9.793 \times 10^{-4}$ N KHP plus 20.0 mL $CO_2$-free deionized water are titrated with approximately 0.01N NaOH. The titration data and appropriate Gran function values are given in the table below.

| Volume NaOH (mL) | pH | $F_{3b} (\times 10^{-3})$ |
|---|---|---|
| 0.000 | 4.59 | |
| 0.050 | 4.78 | |
| 0.100 | 4.97 | 3.90 |
| 0.150 | 5.14 | 3.39 |
| 0.200 | 5.31 | 2.86 |
| 0.250 | 5.48 | 2.34 |
| 0.300 | 5.66 | 1.82 |
| 0.350 | 5.87 | 1.29 |
| 0.400 | 6.14 | 0.79 |
| 0.450 | 6.66 | 0.26 |
| 0.500 | 8.99 | -0.25 |
| 0.700 | 9.95 | -2.29 |
| 0.900 | 10.23 | -4.40 |
| 1.100 | 10.39 | |
| 1.300 | 10.51 | |

The Gran function $F_{3b}$ is calculated for data with pH 5-10. $F_{3b}$ is calculated by

$$F_{3b} = (V + V_s) \left[ \frac{V_s C}{(V_s + V)} \left( \frac{([H^+]K_1 + 2[H^+]^2)}{([H^+]^2 + [H^+]K_1 + K_1K_2)} \right) + [H^+] - \frac{Kw}{[H^+]} \right]$$

$V$ = Volume NaOH added
$V_s$ = Initial sample volume = 25.00 mL
$C$ = N KHP/5 = $1.9586 \times 10^{-4}$
$[H^+]$ = $10^{-pH}$
$K_1$ = $1.3 \times 10^{-3}$
$K_2$ = $3.9 \times 10^{-6}$
$K_w$ = $1.01 \times 10^{-14}$

$F_{3b}$ versus V is plotted in Figure C-2. The data lie on a straight line with the equation $F_3 = a + bV$. The coefficients are calculated using linear regression. From the regression,

$r$ = 1.0000
$a$ = 0.004931 ± 0.000008
$b$ = -0.01036 ± 0.00002

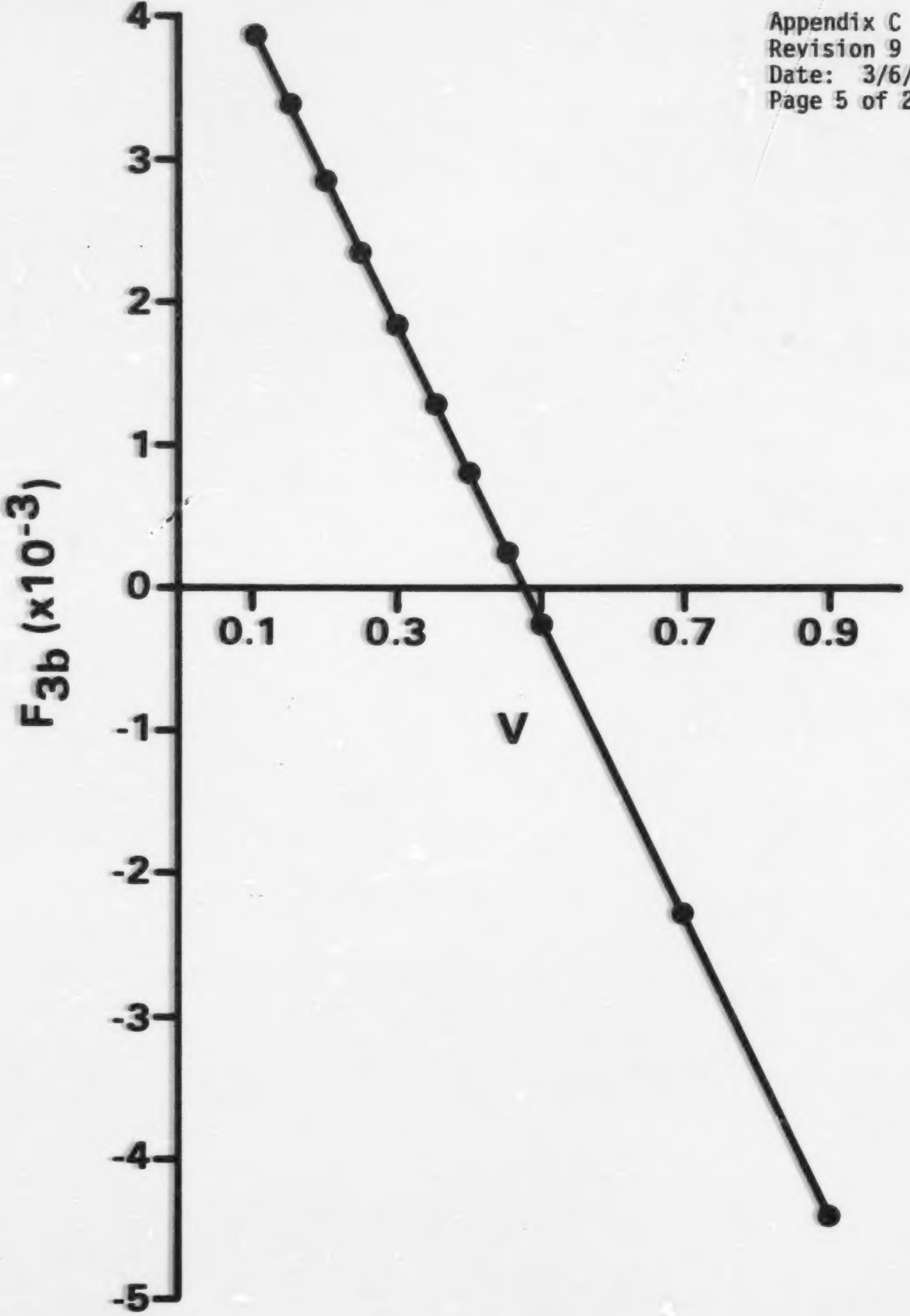

Figure C-2. Plot of $F_{3b}$ versus V for initial NaOH standardization with KHP.

From this $V_3$ and $N_{NaOH}$ are calculated by

$$V_3 = -a/b = 0.4761 \text{ mL}$$

$$N_{NaOH} = \frac{N_{KHP} \times V_{KHP}}{V_3} = 0.01028 \text{ eq/L}$$

## 2.2 Standardization Check (Text Section 4.8.2.2)

0.500 mL of 0.00921N NaOH plus 25.0 mL $CO_2$-free deionized water is titrated with 0.0101N HCl (standardized with $Na_2CO_3$). The titration data and appropriate Gran function values are given in the table below.

| Volume HCl (mL) | pH | $F_1$ ($\times 10^{-3}$) |
|---|---|---|
| 0.000 | 10.29 | |
| 0.100 | 10.15 | |
| 0.200 | 10.03 | 2.75 |
| 0.250 | 9.91 | 2.09 |
| 0.300 | 9.78 | 1.55 |
| 0.350 | 9.60 | 1.03 |
| 0.400 | 9.34 | 0.57 |
| 0.450 | 8.39 | 0.064 |
| 0.500 | 4.76 | -0.45 |
| 0.550 | 4.44 | -0.94 |
| 0.600 | 4.26 | -1.43 |
| 0.650 | 4.12 | -1.98 |
| 0.700 | 4.04 | -2.39 |
| 0.800 | 3.88 | |

The Gran function $F_1$ is determined for data in the pH range 4-10. $F_1$ is calculated by

$$F_1 = (V + V_s) \left( \frac{K_w}{[H^+]} - [H^+] \right)$$

$V$ = volume of HCl added
$V_s$ = initial sample volume = 25.5 mL
$[H^+]$ = $10^{-pH}$
$K_w$ = $1.0 \times 10^{-14}$

$F_1$ versus V is plotted in Figure C-3. The data are on a straight line with the equation $F_1 = a + bV$. The coefficients, determined by linear regression, are

r = 0.9994
a = 0.00465 ± 0.00005
b = -0.01016 ± 0.00011

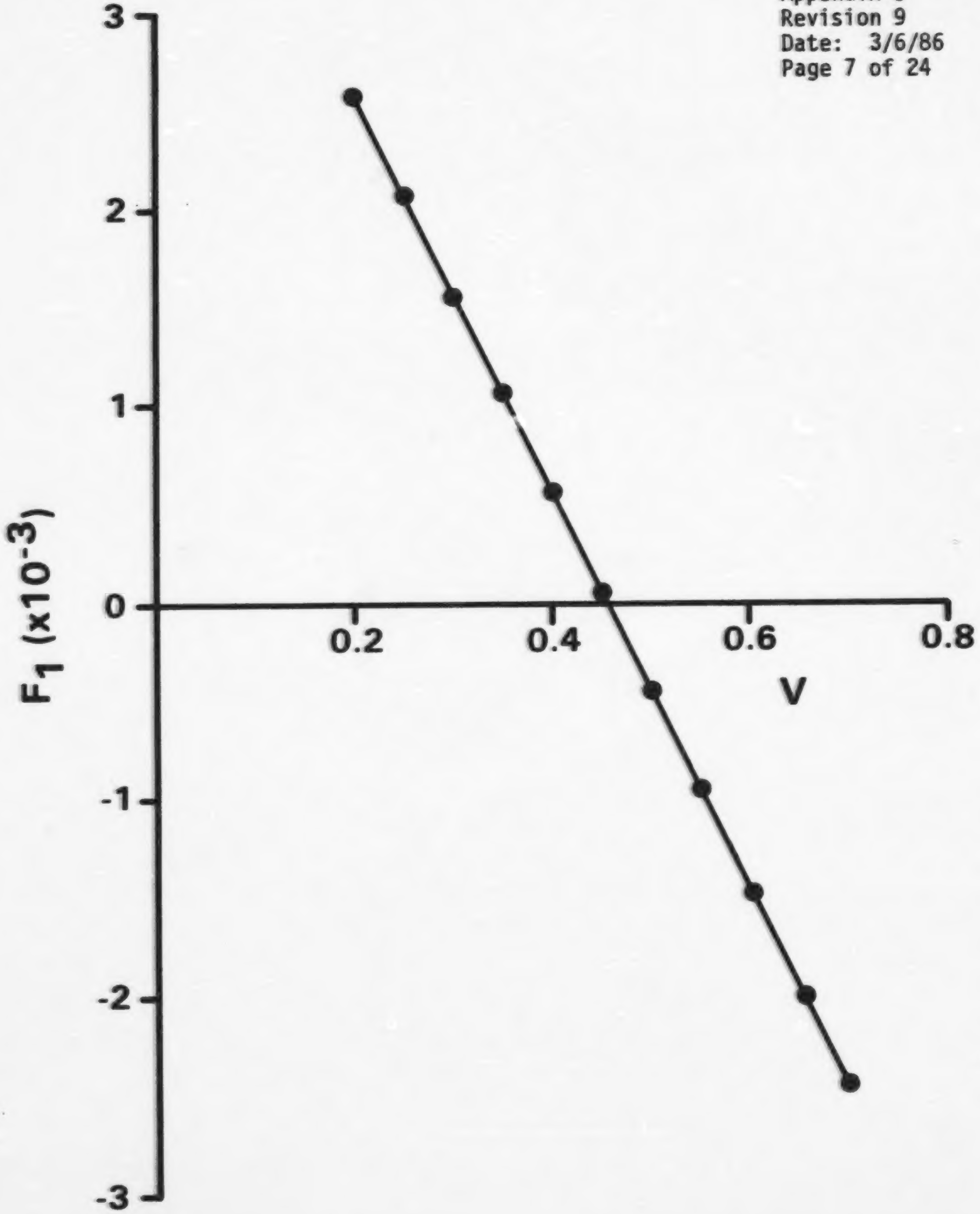

Figure C-3. Plot of $F_1$ versus V for standardization check-titration of NaOH with HCl.

From these values, $V_1$ and $N'_{HCl}$ are calculated by

$$V_1 = -a/b = 0.4577$$

$$N'_{HCl} = \frac{N_{NaOH} \times V_{NaOH}}{V_1} = 0.01006$$

Comparing this value for $N'_{HCl}$ with the previously determined value of $N_{HCl}$, the absolute RPD is

$$\text{RPD in } N_{HCl} \text{ values} = \left| \frac{0.01006 - 0.0101}{0.5\,(0.0101 + 0.01006)} \right| \times 100 = 0.4\%$$

This RPD is acceptable since it is less than 5%.

## 2.3 Routine NaOH Standardization with Standardized HCl (Text Section 4.8.2.3)

1.000 mL of an approximately 0.01N NaOH solution plus 25.00 mL of $CO_2$-free deionized water is titrated with 0.009830N HCl. The titration data are given below.

| mL HCl added | pH | mL HCl added | pH | mL HCl added | pH |
|---|---|---|---|---|---|
| 0.00 | 10.44 | 0.750 | 5.35 | 1.200 | 3.78 |
| 0.200 | 10.30 | 0.800 | 4.65 | 1.400 | 3.62 |
| 0.400 | 10.13 | 0.850 | 4.37 | | |
| 0.600 | 9.71 | 0.900 | 4.22 | | |
| 0.650 | 9.51 | 1.000 | 4.02 | | |
| 0.700 | 9.19 | 1.100 | 3.88 | | |

$F_1$ is calculated for each data pair (V, pH) with a pH 4-10 using the equation

$$F_1 = (V_s + V)\left(\frac{K_w}{[H^+]} - [H^+]\right)$$

where

$V_s$ = initial sample volume = 25.00 + 1.00 = 26.00 mL
$V$ = volume of HCl added.
$[H^+]$ = $10^{-pH}$
$K_w$ = $1.0 \times 10^{-14}$

The new data pairs ($V$, $F_1$) are tabulated below.

| V | $F_1$ (x $10^{-3}$) | V | $F_1$ (x $10^{-3}$) |
|---|---|---|---|
| 0.400 | 3.56 | 0.850 | -1.14 |
| 0.600 | 1.36 | 0.900 | -1.62 |
| 0.650 | 0.86 | 1.000 | -2.58 |
| 0.700 | 0.41 | 1.100 | -3.57 |
| 0.750 | -0.12 | | |
| 0.800 | -0.60 | | |

A plot of $F_1$ versus V is shown in Figure C-4. The data sets corresponding to volumes from V = 0.40 to V = 1.10 lie on a straight line with the equation

$$F_1 = a + bV$$

The coefficients are obtained by linear regression. The results are

$r = 0.9996$
$a = 0.007488 \pm 0.00008$
$b = -0.0101 \pm 0.0001$

From these results,

$V_1 = -a/b = 0.741$

$$N_{NaOH} = \frac{N_{HCl} \times V_1}{V_{NaOH}} = \frac{(0.009830)\ (0.741)}{1.000} = 0.00728$$

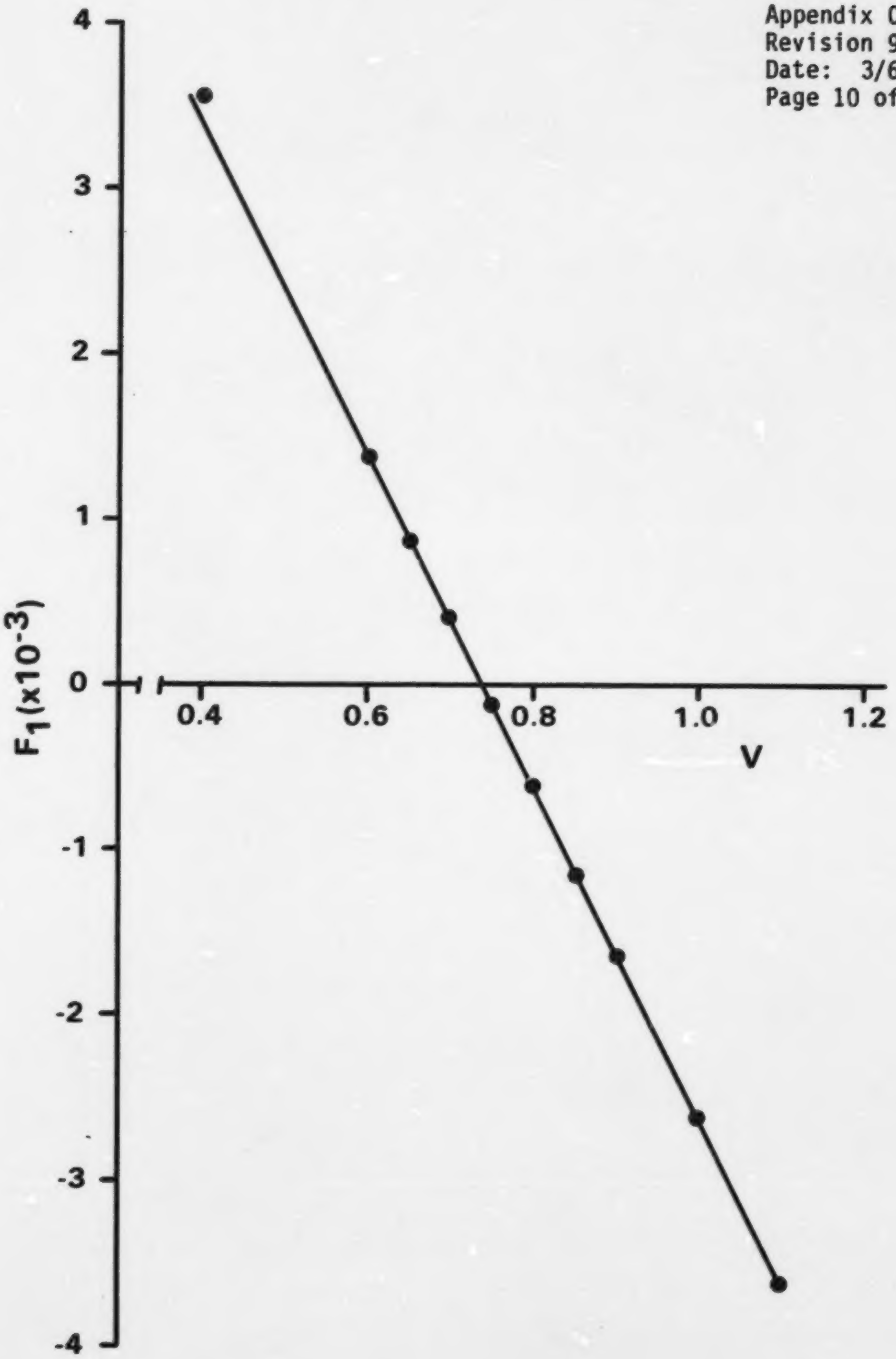

Figure C-4. Plot of $F_1$ versus V for routine NaOH standardization.

## 3.0 ELECTRODE CALIBRATION (TEXT SECTION 4.8.3)

This section describes the electrode calibration procedure. The tables below (A and B) tabulate both the titration data (V and pH), the calculated pH values (pH*), and the coefficients for the line pH = a + b pH*.

TABLE A. ACID TITRATION

$V_S$ = 50.50 mL    $N_{HCl}$ = 0.00983

| Volume HCl (mL) | pH | pH* | Volume HCl (mL) | pH | pH* |
|---|---|---|---|---|---|
| 0.000 | 5.87 | --- | 0.450 | 4.05 | 4.06 |
| 0.025 | 5.25 | 5.31 | 0.500 | 4.00 | 4.02 |
| 0.050 | 4.97 | 5.01 | 0.600 | 3.92 | 3.94 |
| 0.100 | 4.68 | 4.71 | 0.800 | 3.80 | 3.81 |
| 0.150 | 4.51 | 4.54 | 1.000 | 3.71 | 3.72 |
| 0.200 | 4.38 | 4.41 | 1.200 | 3.64 | 3.64 |
| 0.250 | 4.29 | 4.31 | 1.500 | 3.55 | 3.55 |
| 0.300 | 4.22 | 4.24 | 1.700 | 3.50 | 3.50 |
| 0.350 | 4.15 | 4.17 | 2.000 | 3.43 | 3.43 |
| 0.400 | 4.10 | 4.11 | | | |

r = 1.00    a = 0.10 ± 0.01    b = 0.971 ± 0.002

TABLE B. BASE TITRATION

$V_S$ = 40.4 mL    $N_{NaOH}$ = 0.00804

| Volume NaOH (mL) | pH | pH* | Volume NaOH (mL) | pH | pH* |
|---|---|---|---|---|---|
| 0.000 | 6.66 | --- | 0.820 | 10.18 | 10.20 |
| 0.050 | 9.03 | 9.00 | 0.940 | 10.25 | 10.26 |
| 0.200 | 9.55 | 9.60 | 1.080 | 10.31 | 10.32 |
| 0.300 | 9.66 | 9.77 | 1.200 | 10.36 | 10.37 |
| 0.400 | 9.75 | 9.90 | 1.300 | 10.40 | 10.40 |
| 0.500 | 9.90 | 9.99 | 1.400 | 10.43 | 10.43 |
| 0.600 | 10.00 | 10.07 | 1.500 | 10.47 | 10.46 |

r = 0.99    a = 0.08 ± 0.27    b = 0.99 ± 0.03

The data in Tables A and B are plotted in Figure C-5. Except for two points in the base titration (at $V = 0.3$ and $0.4$), the data lie on a straight line. (The lines calculated for each titration are essentially coincident as indicated by their coefficients.) Excluding these two points, the data are fit to the line with the equation $pH = a + b\,pH^*$. The coefficients of the line (obtained by linear regression) are

$r = 1.0000$
$a = -0.014 \pm 0.0011$
$b = 0.999 \pm 0.002$

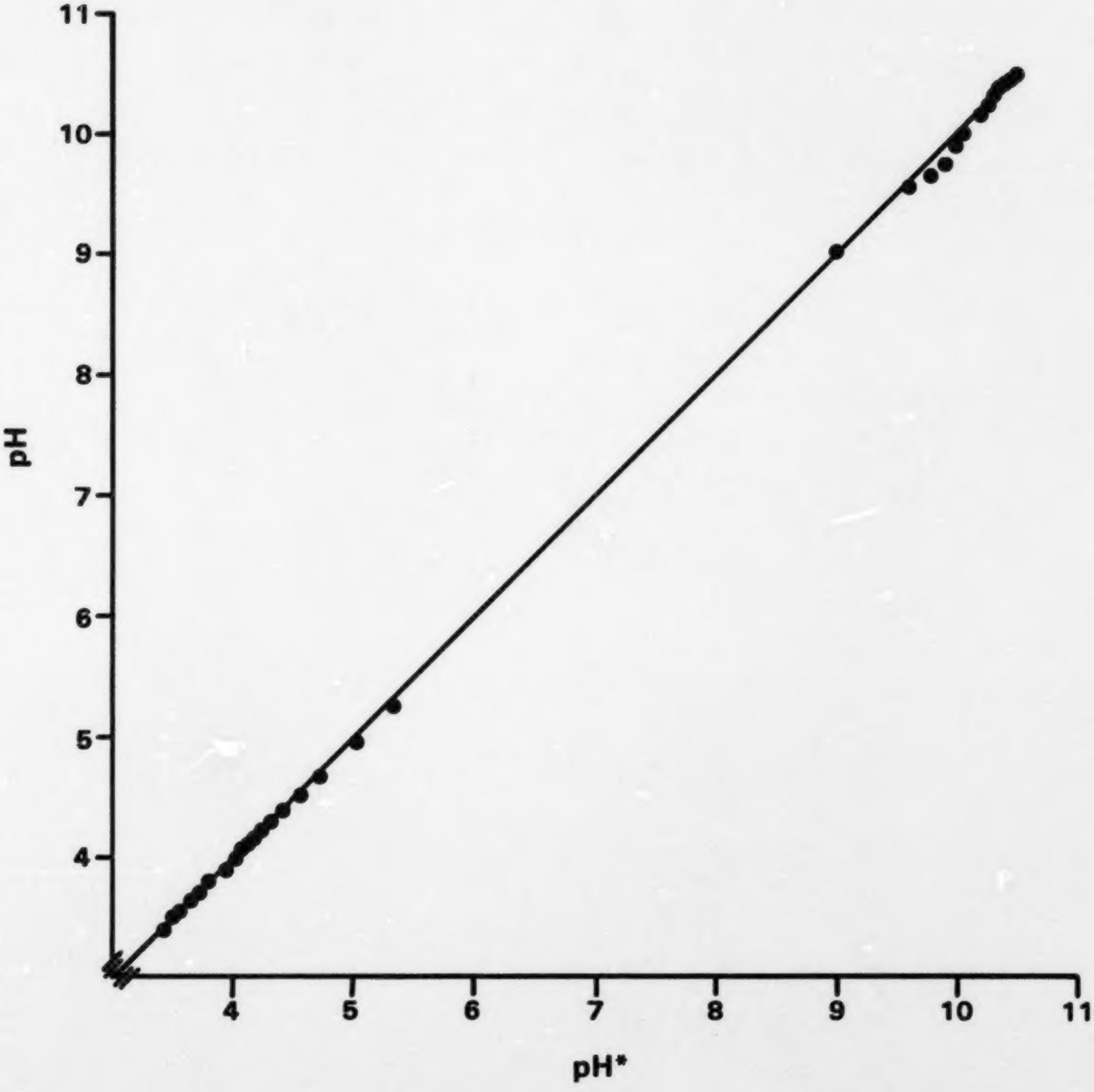

Figure C-5. Plot of pH* versus pH for electrode calibration.

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## 4.0 BLANK ANALYSIS - ALKALINITY DETERMINATION (TEXT SECTIONS 4.9.2 and 4.11.1)

This section describes the determination of alkalinity in a blank solution. The blank is prepared by adding 0.40 mL of 0.10M NaCl to 40.00 mL deionized water. It is titrated with 0.00983N HCl. The titration data are given below (both measured and calculated pH* values are included).

| Volume HCl (mL) | pH | pH* | $F_1$ | Volume HCl (mL) | pH | pH* | $F_1$ |
|---|---|---|---|---|---|---|---|
| 0.000 | 5.84 | 5.85 | | 0.500 | 3.91 | 3.91 | 0.00503 |
| 0.080 | 4.69 | 4.70 | | 0.600 | 3.84 | 3.84 | 0.00593 |
| 0.120 | 4.52 | 4.53 | | 0.700 | 3.77 | 3.77 | 0.00698 |
| 0.200 | 4.31 | 4.32 | 0.00194 | 1.000 | 3.62 | 3.62 | 0.00993 |
| 0.300 | 4.14 | 4.14 | 0.00295 | 1.200 | 3.55 | 3.55 | 0.0117 |
| 0.400 | 4.01 | 4.02 | 0.00390 | 1.500 | 3.45 | 3.45 | 0.0149 |

The Gran function $F_{1a}$ ($F_{1a} = (V_s + V)[H^+]$) is calculated for pH* value less than 4.5 and the values included in the table.

$F_1$ versus V is plotted in Figure C-6. The data are linear and fit the line
$F_1 = a + bV$ using linear regression. The resulting coefficients are

$r = 0.9998$
$a = (-0.70 \pm 5.6) \times 10^{-5}$
$b = 0.00989 \pm 0.00007$

From this,

$$V_1 = -a/b = 7.05 \times 10^{-4} \text{ mL}$$

$$[\text{Alk}] = \frac{V_1 C_{HCl}}{V_{sa}} = 1.7 \times 10^{-7} \frac{\text{eq}}{\text{L}} = 0.17\ \mu\text{eq/L}$$

This value for [Alk] is acceptable.

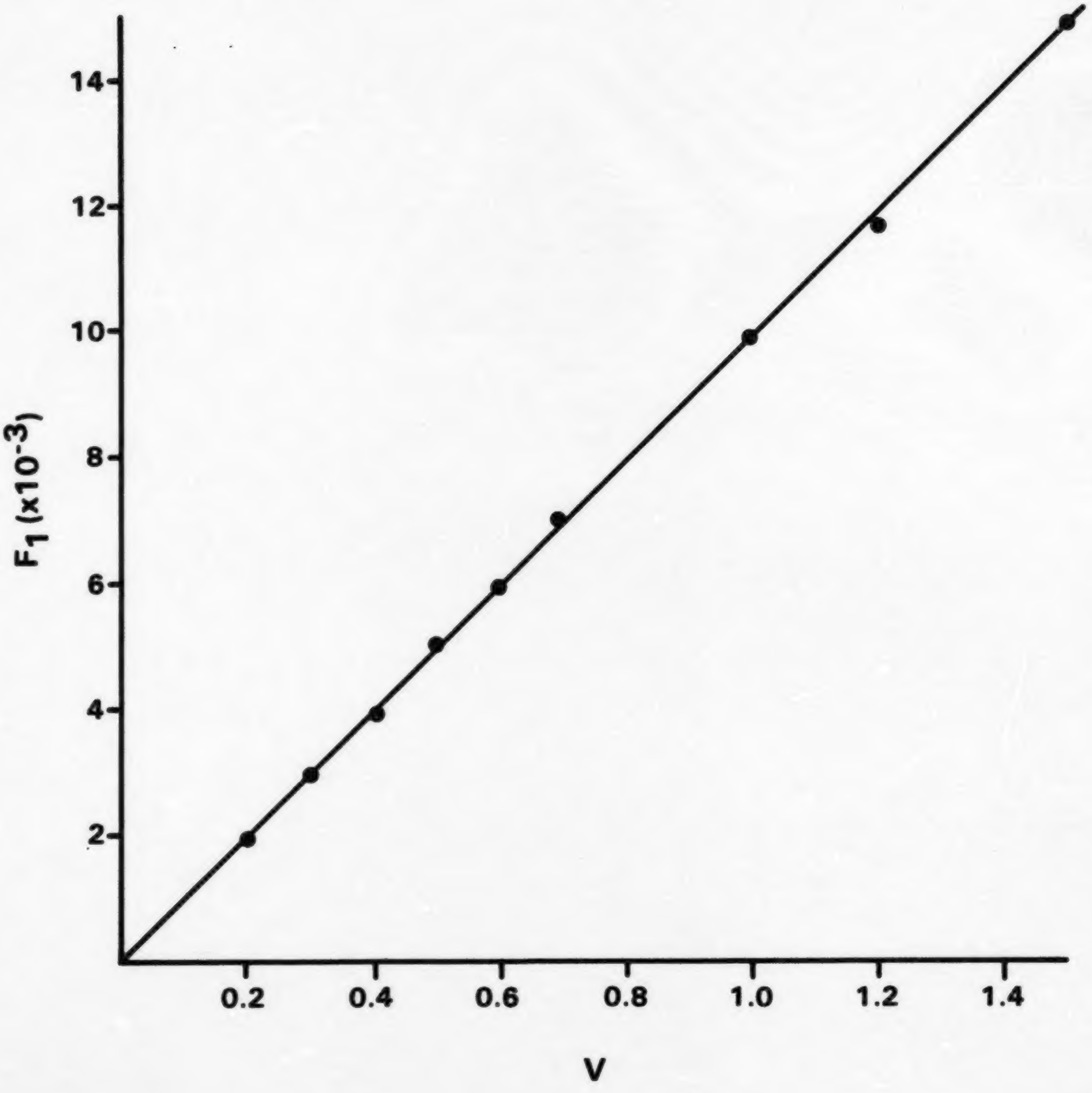

Figure C-6. Plot of $F_{1a}$ versus V for alkalinity determination of blank.

## 5.0 SAMPLE ANALYSIS

### 5.1 Titration Data

A natural lake sample was titrated as described in section 4.10 of the text. The titration data are given below. Also included are values for the calculated pH (pH*).

Acid Titration

$V_{sa}$ = 40.00 mL $V_{salt}$ = 0.40 mL
$C_a$ = 0.00983 eq/L

| $V_a$ | pH | pH* | $V_a$ | pH | pH* |
|---|---|---|---|---|---|
| 0.000 | 5.10 | 5.11 | 0.460 | 3.99 | 3.99 |
| 0.040 | 4.89 | 4.90 | 0.550 | 3.91 | 3.91 |
| 0.080 | 4.71 | 4.72 | 0.650 | 3.84 | 3.84 |
| 0.120 | 4.56 | 4.57 | 0.750 | 3.77 | 3.77 |
| 0.140 | 4.50 | 4.51 | 0.900 | 3.69 | 3.69 |
| 0.160 | 4.44 | 4.44 | 1.100 | 3.61 | 3.61 |
| 0.260 | 4.24 | 4.24 | 1.400 | 3.50 | 3.50 |
| 0.280 | 4.21 | 4.21 | 1.700 | 3.42 | 3.42 |
| 0.380 | 4.08 | 4.08 | | | |

Base Titration

$V_{sb}$ = 40.00 mL $V_{salt}$ = 0.40 mL
$C_b$ = 0.00702 eq/L

| $V_b$ | pH | pH* | $V_b$ | pH | pH* |
|---|---|---|---|---|---|
| 0.00 | 5.08 | 5.09 | 0.425 | 8.30 | 8.32 |
| 0.015 | 5.13 | 5.14 | 0.470 | 8.66 | 8.68 |
| 0.030 | 5.26 | 5.27 | 0.500 | 8.85 | 8.87 |
| 0.050 | 5.35 | 5.36 | 0.540 | 9.01 | 9.03 |
| 0.080 | 5.57 | 5.58 | 0.560 | 9.10 | 9.12 |
| 0.120 | 5.78 | 5.79 | 0.600 | 9.21 | 9.23 |
| 0.160 | 6.06 | 6.07 | 0.660 | 9.35 | 9.37 |
| 0.200 | 6.30 | 6.31 | 0.700 | 9.44 | 9.47 |
| 0.240 | 6.65 | 6.66 | 0.780 | 9.57 | 9.60 |
| 0.280 | 6.98 | 7.00 | 0.900 | 9.72 | 9.75 |
| 0.320 | 7.29 | 7.31 | 1.000 | 9.83 | 9.86 |
| 0.340 | 7.46 | 7.48 | 1.100 | 9.92 | 9.95 |
| 0.360 | 7.62 | 7.64 | 1.405 | 10.12 | 10.15 |
| 0.380 | 7.83 | 7.85 | 1.700 | 10.26 | 10.29 |
| 0.400 | 8.03 | 8.05 | 2.200 | 10.43 | 10.43 |
| | | | 2.500 | 10.51 | 10.54 |

## 5.2 Initial Estimate of $V_1$ (Text Section 4.11.1)

The Gran function $F_{1a}$ is calculated for each data pair from the acid titration with a pH* <4. The values are given in the table below.

| $V_a$ | $F_{1a}(\times 10^{-3})^*$ | $V_a$ | $F_{1a}(\times 10^{-3})^*$ |
|---|---|---|---|
| 0.460 | 4.18 | 0.900 | 8.43 |
| 0.550 | 5.04 | 1.100 | 10.2 |
| 0.650 | 5.93 | 1.400 | 13.2 |
| 0.750 | 6.99 | 1.700 | 16.0 |

$^*F_{1a} = (V_a + V_s)\,[H^+]$

$F_{1a}$ versus $V_a$ is plotted in Figure C-7. A regression of $F_{1a}$ on $V_a$ is performed to fit the data to the line $F_{1a} = a + bV$. The resulting coefficients are:

$r = 0.9999$
$a = -0.000217 \pm 0.000050$
$b = 0.009548 \pm 0.000048$

From this, the initial estimate of $V_1$ is calculated by

$$V_1 = -a/b = 0.0227 \text{ mL}$$

Since $V_1 > 0$ and the initial sample pH* $\leq 7.6$, calculation procedure B (Text Section 4.11.3) is used to determine the Alk and Acy of the sample.

## 5.3 Initial Estimates of $V_2$, Alk, Acy, and C (Text Section 4.11.3, step 1)

From the base titration data, $V_2$ is estimated to be 0.40 mL (the first point with a pH* $\leq 8.2$). Now that initial estimates of $V_1$ and $V_2$ have been obtained, estimates of Alk, Acy, and C can be calculated.

$$\text{Alk} = \frac{V_1\ C_a}{V_{sa}} = 5.6 \times 10^{-6} \text{ eq/L}$$

$$\text{Acy} = \frac{V_2\ C_b}{V_{sb}} = 7.02 \times 10^{-5} \text{ eq/L}$$

$$C = \text{Alk} + \text{Acy} = 7.58 \times 10^{-5} \text{ eq/L}$$

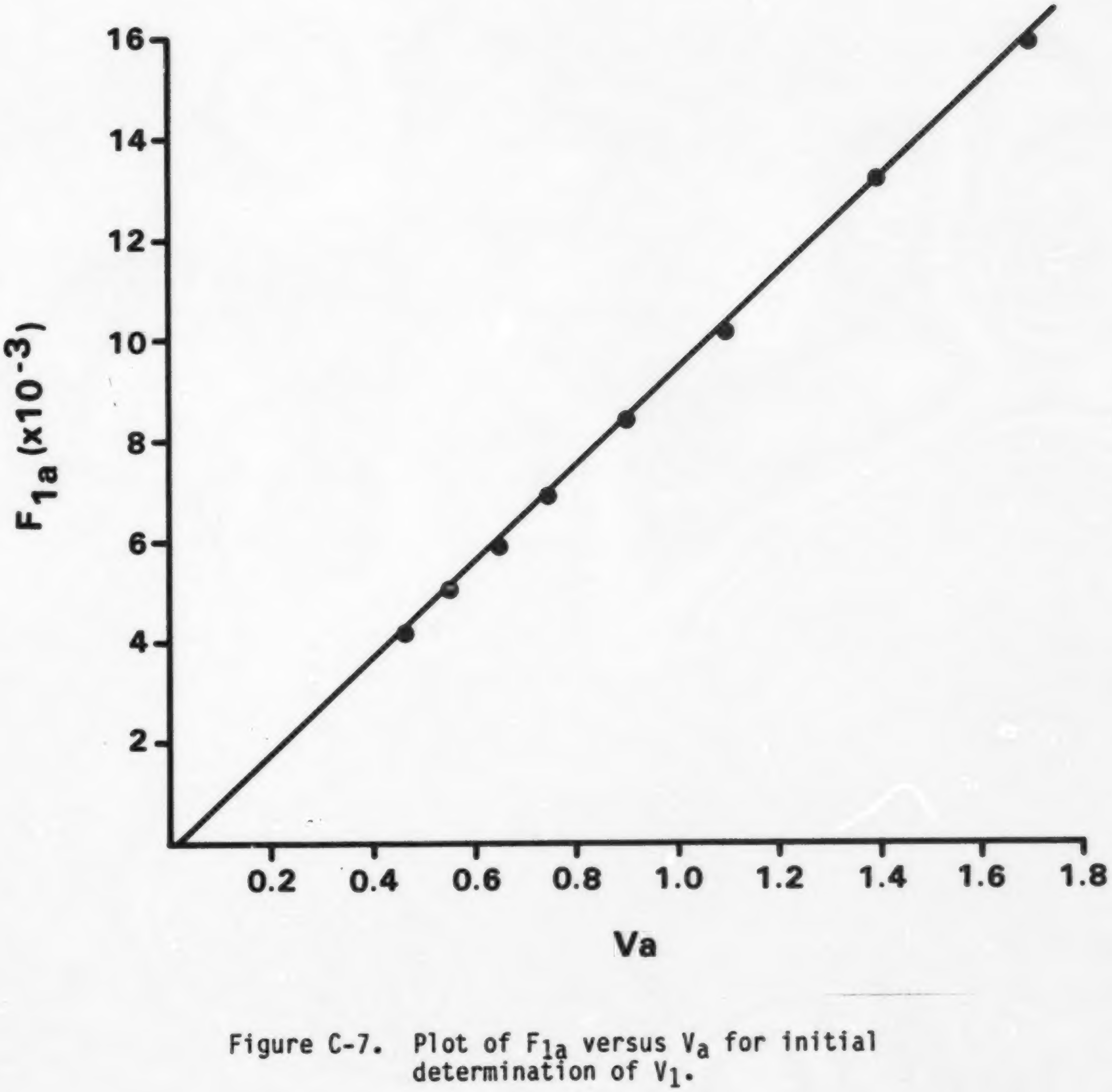

Figure C-7. Plot of $F_{1a}$ versus $V_a$ for initial determination of $V_1$.

## 5.4 Refined Estimates of $V_1$ and $V_2$ (Text Section 4.11.3, step 2)

The Gran function $F_{1c}$ (Equation 1, section 4.11.1.3) is calculated for acid titration data with volumes across the current estimate of $V_1$. The values are given below.

| $V_a$ | $F_{1c}(x10^{-4})$ | $V_a$ | $F_{1c}(x10^{-4})$ |
|---|---|---|---|
| 0.000 | -1.68 | 0.160 | -14.4 |
| 0.040 | -4.10 | 0.260 | -23.2 |
| 0.080 | -7.05 | 0.280 | -24.9 |
| 0.120 | -10.4 | 0.380 | -33.8 |
| 0.140 | -12.1 | | |

$F_{1c}$ versus $V_a$ is plotted in Figure C-8. A regression of $F_{1b}$ on $V_a$ is performed. The regression results are

$r = 0.999$
$a = -0.00006 \pm 0.00003$
$b = -0.00864 \pm 0.00016$

A new estimate of $V_1$ is

$$V_1 = -a/b = -0.007 \text{ mL}$$

Next the Gran function $F_{2c}$ (Equation 2, text section 4.11.1.3) is calculated from data sets from the base titration with volumes across the current estimate of $V_2$. The values are given below.

| $V_b$ | $F_{2c}(x\ 10^{-4})$ | $V_b$ | $F_{2c}(x\ 10^{-4})$ |
|---|---|---|---|
| 0.340 | 1.99 | 0.470 | -2.60 |
| 0.360 | 1.28 | 0.500 | -4.14 |
| 0.380 | .555 | 0.540 | -6.03 |
| 0.400 | -0.031 | 0.560 | -7.43 |
| 0.425 | -.868 | 0.600 | -9.55 |

$F_{2c}$ versus $V_b$ is plotted in Figure C-9. A regression of $F_{2c}$ on $V_b$ is performed. (Data with $V_b$ >0.5 are not used in the regression.) The regression results are

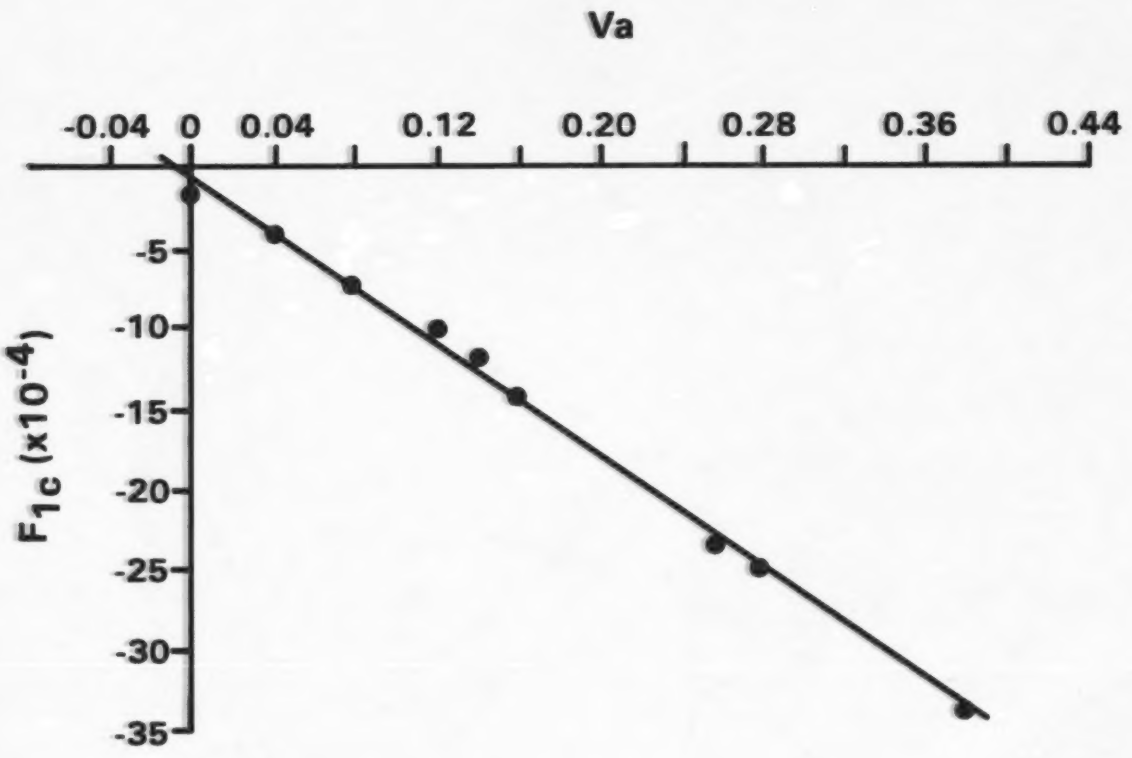

Figure C-8. Plot of $F_{1c}$ versus $V_a$ for $V_1$ determination.

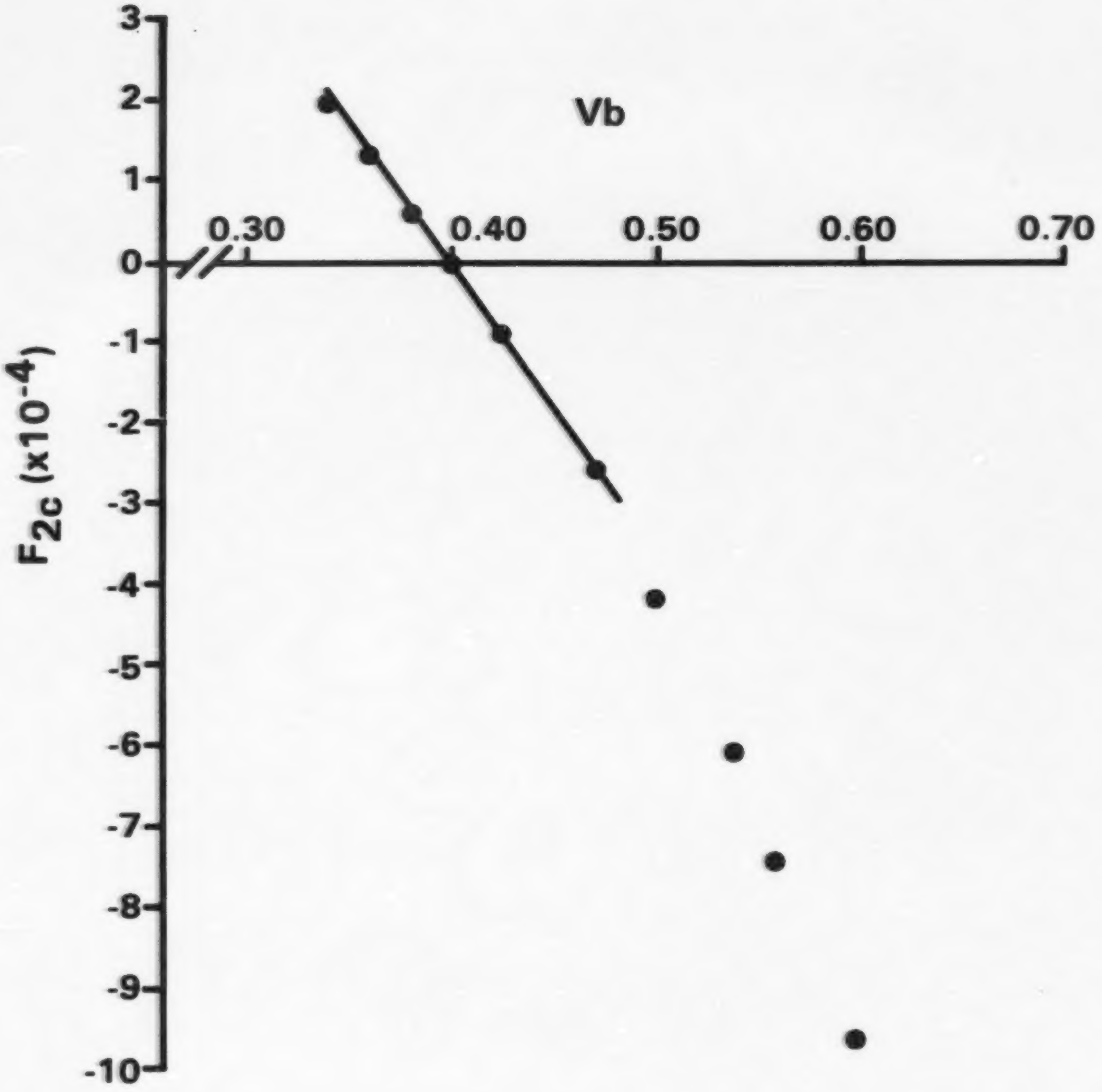

Figure C-9. Plot of $F_{2c}$ versus $V_b$ for $V_2$ determination.

$r = 0.999$
$a = 0.00135 \pm 0.000024$
$b = -0.003400 \pm 0.000060$

A new estimate of $V_2$ is

$$V_2 = -a/b = 0.398 \text{ mL}$$

## 5.5 New Estimates of Alk, Acy, and C (Text Section 4.11.3, step 3)

From the new estimates of $V_1$ and $V_2$, new estimates of Alk, Acy, and C are calculated.

$$\text{Alk*} = \frac{V_1 C_a}{V_{sa}} = -1.5 \times 10^{-6} \text{ eq/L}$$

$$\text{Acy*} = \frac{V_2 C_b}{V_{sb}} = 6.98 \times 10^{-5} \text{ eq/L}$$

$$C^* = \text{Alk} + \text{Acy} = 6.83 \times 10^{-5} \text{ eq/L}$$

## 5.6 Comparison of Latest Two Estimates of Total Carbonate (Text Section 4.11.3, step 4)

$$\left|\frac{C - C^*}{C + C^*}\right| = 0.041 > 0.001$$

Since C and C* do not agree, a new C is calculated from their average

$$C(\text{new}) = (C + C^*)/2 = 7.09 \times 10^{-5} \text{ eq/L}$$

The calculations in sections 5.4 through 5.6 of this appendix are repeated until successive iterations yield total carbonate values which meet the above criteria. The results from each iteration (including those already given) are given below.

| Iteration | $V_1$(mL) | $V_2$(mL) | Alk (µeq/L) | Acy (µeq/L) | C (µeq/L) | $\frac{C - C^*}{C + C^*}$ | New C (µeq/L) |
|---|---|---|---|---|---|---|---|
| 1 | 0.0227 | 0.400 | 5.6 | 70.2 | 75.8 | - | - |
| 2 | -0.0060 | 0.398 | -1.5 | 69.9 | 68.4 | 0.051 | 72.1 |
| 3 | -0.0067 | 0.397 | -1.6 | 69.7 | 68.1 | 0.029 | 70.1 |
| 4 | -0.0071 | 0.397 | -1.7 | 69.7 | 67.9 | 0.016 | 69.0 |
| 5 | -0.0072 | 0.396 | -1.8 | 69.6 | 67.8 | 0.009 | 68.4 |
| 6 | -0.0074 | 0.396 | -1.8 | 69.5 | 67.7 | 0.005 | 68.1 |
| 7 | -0.0074 | 0.396 | -1.8 | 69.5 | 67.7 | 0.003 | 67.9 |
| 8 | -0.0074 | 0.396 | -1.8 | 69.5 | 67.7 | 0.001 | 67.8 |
| 9 | -0.0074 | 0.396 | -1.8 | 69.5 | 67.7 | 0.008 | - |

The final values for Alk and Acy are reported on Form 11.

## 6.0 QUALITY CONTROL CALCULATIONS

Examples of the QC calculations are described in this section.

### 6.1 Comparison of Calculated Alkalinity and Measured Alkalinity (Text Section 4.9.5)

For the sample analyzed in section 5.0 of this appendix, the following data were obtained.

| | |
|---|---|
| initial pH = 5.09 | air-equilibrated pH = 5.06 |
| DIC = 0.59 mg/L | air-equilibrated DIC = 0.36 |

From these data, the calculated Alk values are computed using the equation

$$[\mathrm{Alk}]_C\ (\mu\mathrm{eq/L}) = \left[\frac{\mathrm{DIC}}{12011}\left(\frac{[\mathrm{H}^+]K_1 + 2K_1\,K_2}{[\mathrm{H}^+]^2 + [\mathrm{H}^+]K_1 + K_1\,K_2}\right) + \frac{\mathrm{Kw}}{[\mathrm{H}^+]} - [\mathrm{H}^+]\right] \times 10^6$$

The results are

$[\mathrm{Alk}]_{C1} = -5.6\ \mu\mathrm{eq/L}$ $\qquad$ $[\mathrm{Alk}]_{C2} = -7.2\ \mu\mathrm{eq/L}$

Then

$$|[\mathrm{Alk}]_{C1} - [\mathrm{Alk}]_{C2}| = 1.6\ \mu\mathrm{eq/L} < 15\ \mu\mathrm{eq/L}$$

Since $[\mathrm{Alk}]_{C1}$ and $[\mathrm{Alk}]_{C2}$ are in agreement, their average value is used for comparison to the measured value.

$[\mathrm{Alk}]_{C\text{-avg}} = -6.4\ \mu\mathrm{eq/L}$ $\qquad$ $\mathrm{Alk} = -1.8\ \mu\mathrm{eq/L}$

$$D = |\mathrm{Alk}_C - \mathrm{Alk}| = 4.6\ \mu\mathrm{eq/L} < 15\ \mu\mathrm{eq/L}$$

The calculated and measured Alk values agree, which backs up the assumption of a carbonate system.

### 6.2 Comparison of Calculated Acidity and Measured Acidity (Text Section 4.9.6)

For the sample analyzed in section 5.0 of this appendix, the following data were obtained.

initial pH = 5.09

DIC = 0.59 mg/L

Acy = 69.0 μeq/L

From these data, the Acy is computed using the equation

$$[\mathrm{Alk}]_C\ (\mu eq/L) = \left[\frac{DIC}{12011}\left(\frac{[H^+]^2 - K_1\ K_2}{[H^+]^2 + [H^+]K_1 + K_1\ K_2}\right) + [H^+] - \frac{K_w}{[H^+]}\right] \times 10^6$$

The result is

$$[\mathrm{Acy}]_C = 54.7\ \mu eq/L$$

This value is compared to the measured value.

$$D = [\mathrm{Acy}]_C - \mathrm{Acy} = -14.7\ \mu eq/L < -10\ \mu eq/L$$

Although borderline, this value of D is indicative of other protolytes in the system which are contributing to the measured Acy. This might be expected since the sample also contains 3.2 mg/L DOC.

### 6.3 Comparison of Calculated Total Carbonate and Measured Total Carbonate (Text Section 4.9.7)

For the sample analyzed in section 5.0 of this appendix, the following data were obtained.

initial pH = 5.09
Acy = 69.5 μeq/L = 69.5 μmole/L
DIC = 0.59 mg/L
Alk = -1.8 μeq/L = -1.8 μmole/L

From the DIC value, the total carbonate is calculated.

$$C_C = 83.26 \times DIC = 49.1\ \mu mole/L$$

This calculated value is then compared to the measured value.

$$D = C_C - (\mathrm{Alk} + \mathrm{Acy}) = -18.6\ \mu mole/L < -10\ \mu mole/L$$

Although borderline, this value of D is indicative of other protolytes in the system. This might be expected since the sample also contains 3.2 mg/L DOC. Notice that the same conclusion was reached in the Acy comparison.

In general, noncarbonate protolytes are significant (i.e., contribute significantly to the total protolyte concentration), when indicated by one (or both) of the individual comparisons (Alk and Acy comparisons) and the total carbonate comparison.